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PROCEEDINGS OF THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

The Relationship between the “Solar Constant” and Terrestrial Magnetism.

By C. CHREE, Sc.D., LL.D., F.R.S.

(Received June 22, 1925.)

§ 1. The issue of an authoritative list of provisional values of the “solar constant” as determined by Dr. C. G. Abbot* and colleagues, for the period August, 1920, to November, 1924, is of interest to all who concern themselves with solar radiation and its relation to terrestrial phenomena. What interests myself is the possible connection between fluctuations of the “solar constant” and the phenomena of Terrestrial Magnetism. As is well known, the solar 11-year period is prominent in the range of the regular diurnal variation of the earth’s magnetic field, and the sun’s rotation period—approximately 27 days† in the sunspot zone—is recognisable in magnetic disturbance. Owing to the large annual variation in the range of the magnetic elements, conclusive evidence of a parallelism between the amplitude of that range and the size of the “solar constant” can hardly be hoped for from so short a period as four years. But the 27-day interval is usually easily recognisable in the magnetic data from a single year, and if there is any at all intimate relation between the value of the “solar constant” and the earth’s magnetic condition, either on the same day or on a definite subsequent day—i.e., a day 1 ..., 5 or 10 days later—then we should expect a 27-day interval to show itself in Abbot’s figures. The data now published seem ample to check this point, if treated in the way which has proved successful in the case of magnetic phenomena and sunspot numbers or areas. We start by taking for each month a certain number of days selected as those in which the element under investigation

* ‘Provisional Solar-constant Values, August, 1920, to November, 1924.’ By C. G. Abbot and colleagues. Smithsonian Institution, Washington, Feb., 1925.

† ‘Roy. Soc. Proc.,’ A, vol. 101, p. 368.

has its largest values, and an equal number selected as the days in which the aforesaid element has its smallest values. We then compare the mean value of the element for two associated groups of days. The days of the one associated group follow the days of the first primary group of selected days by, say, 26, 27 and 28 days. The days of the second associated group similarly follow the days of the second primary group of selected days. If the representative day in either of the primary groups be described as day n , then the representative days in the associated groups will be respectively $n + 26$, $n + 27$ and $n + 28$. The so-called 27-day interval is not a sharply defined interval, such as 27.00 days. For one thing, magnetic storms usually extend to more than one (Greenwich) day, and solar phenomena have also their indefiniteness. Thus it is desirable to extend the investigation to at least the two adjacent days.

In the present case the first of the two primary groups of days included the 5 days of each month for which the "solar constant" had its largest values, the second the 5 days for which the "solar constant" had its lowest values. In Abbot's list as published, data are distinguished as S (satisfactory), S₋ (nearly satisfactory), U₊ (rather unsatisfactory) and U₋ (unsatisfactory). Here only S data have been accepted, all data marked U being treated as non-existent. In some months there were a good many blank days, consequently there were often less than five associated days available. To meet this difficulty, the entries made for each month in the columns $n + 26$, $n + 27$ and $n + 28$ represented in each case the mean value derived from all the days available, whether 5, 4, 3 or even 1. In one month no days at all were available for column $n + 28$ in the group associated with the primary group of high "solar constant," and the final mean for this column depended on only 48 instead of 49 months, as in the other columns. There was a like deficiency in the case of columns $n + 27$ and $n + 28$ in the group associated with the days of low "solar constant." While it is only proper to mention this, it is of practically no importance in view of the large number of months available. It will suffice to give the final mean values of the "solar constant" for the four columns :—

Day.	n	$n + 26$	$n + 27$	$n + 28$
Days of high "solar constant" and associated days	1.9431	1.9300	1.9298	1.9298
" " low " " "	1.9184	1.9309	1.9299	1.9303
Algebraic excess of former group	+0.0247	-0.0009	-0.0001	-0.0005

The difference between the representative days of high and low "solar constant"—sometimes termed the primary pulse—is quite substantial, but the differences between the two groups of associated days—sometimes termed the secondary pulse—are insignificant, and, as it happens, are not even of the sign to be expected if a real 27-day interval existed. This accords with the results of an earlier less complete investigation,* which depended on a less authoritative set of "solar constant" values for only two years, 1919 and 1920.

§ 2. It may be suggested that sunspot minimum is an unfavourable time for the 27-day interval to manifest itself. This has not been true of previous sunspot minima, but some direct evidence to the contrary for the present sunspot minimum appeared desirable. Accordingly, the point was investigated for 1923, the actual year of sunspot minimum, employing the international magnetic character figures; 1923, it may be explained, is the latest year for which official character figures are yet available.

As in previous like occasions, a sufficient sequence of primary and associated days was taken to show the form of both primary and secondary pulses. The primary days of the first group included the five international disturbed days of each month, those of the second group included the five international quiet days. For the few associated days which fell in January, 1924, character figures were calculated from the data supplied in the De Bilt lists for the first quarter of that year. With this small exception all the character figures used were extracted from the final De Bilt publication for 1923. The results are as follows:—

Mean Character Figure.

Day.	$n-2$	$n-1$	n	$n+1$	$n+2$	$n+25$	$n+26$	$n+27$	$n+28$	$n+29$	$n+30$
Disturbed and associated days	0.54	0.87	1.21	0.93	0.66	0.43	0.63	0.78	0.71	0.57	0.42
Quiet and associated days	0.37	0.20	0.06	0.29	0.55	0.37	0.31	0.29	0.42	0.61	0.66
Excess for disturbed and associated days	+0.17	+0.67	+1.15	+0.64	+0.11	+0.06	+0.32	+0.49	+0.29	-0.04	-0.24

The mean of the 12 monthly mean character figures was 0.48. The fact that this is exceeded by the difference figure in column $n + 27$ is evidence

* 'Meteorological Magazine,' vol. 58, p. 25 (1923).

of the exceptional vigour of the 27-day interval in 1923. There is, however, admittedly a somewhat abnormal feature in the difference data and the data for the days associated with the quiet days in columns $n + 29$ and $n + 30$. Investigation showed that this arose from the fact that in several months the most disturbed days followed only a day or two after the quietest.

No explanation other than solar action has been suggested for the 27-day interval in terrestrial magnetism. Thus we may reasonably assume that when the 27-day interval is particularly conspicuous on the earth, it is at least normally developed on the sun. The natural inference is that the solar phenomena which occasion the 27-day magnetic interval on the earth are not represented in the daily "solar constant" figures.

§ 3. Another enquiry that suggested itself was whether there was any recognisable relation between the value of the "solar constant" and the magnetic character either on the same day or a subsequent day. The five days of largest and the five days of least "solar constant" were taken out for each month of 1923. This gave 60 days representative of high, and 60 representative of low "solar constant." In each case the corresponding international magnetic character figures were got out for the 60 days described as days n , and for the subsequent days $n + 1$, $n + 2$, $n + 3$ and $n + 4$. It was not considered necessary to go further, but there would, of course, be no difficulty in doing so if it appeared expedient. Presumably the day in Abbot's list is not the Greenwich day, but commences some hours later. But this ought, if anything, to favour the method, because magnetic disturbance tends apparently to prefer Greenwich night. The results obtained for the mean character figure in the several groups of days were as follows :—

Day.	n	$n + 1$	$n + 2$	$n + 3$	$n + 4$
Days of high "solar constant" and associated days	0·39	0·49	0·48	0·46	0·47
„ low „ „ „	0·50	0·51	0·57	0·60	0·55

The only entry in connection with the days of high "solar constant" which is not very close to 0·48, the mean value for the year, is that in column n , and it is *low*. In the days associated with the days of low "solar constant" several of the figures—notably those in columns $n + 3$ and $n + 2$ —do depart very sensibly from the mean for the year, but they are all *high*. Investigation showed that these high values were mainly due to the fact that in several months—notably February and September—there were groups of successive

days of low “solar constant” more or less coincident with groups of days of high magnetic character figure.

§ 4. The previous results are more suggestive of an association of magnetic disturbance with low than with high values of the “solar constant.” But it seems clear from the mean annual values of the “solar constant” that, if any association exists with terrestrial magnetism, it must have the same sign as the association between sunspots and magnetism.

In proof of this we have the following mean annual values :—

Year.	1921.	1922.	1923.
Wolfer’s sunspot frequency	26·1	14·2	5·5 (prov.)
Abbot’s “solar constant”	1·9467	1·9245	1·9233
Declination range, Kew diurnal inequality A	7′·51	6′·55	6′·23
“ “ “ “ B	7′·07	6′·68	5′·87

The Wolfer figure for 1923 is a provisional one given in a paper by Dr. L. A. Bauer.* Of the Kew declination ranges, A is from all ordinary days (*i.e.* all except the highly disturbed), B from the international quiet days.

All the figures show a fall from 1921 to 1922, and again from 1922 to 1923, though the latter is somewhat inconspicuous in the case of the “solar constant.”

Wolfer’s provisional figures usually differ but little from the final ones. If we accept the Wolfer figure for 1923, and compare 1921 with the mean of 1922 and 1923, we have the following results :—

—	Wolfer.	Abbot.	Kew A.	Kew B.
1921	26·1	1·9467	7′·51	7′·07
Mean 1922 and 1923	9·8	1·9239	6′·39	6′·28
Excess of 1921	16·3	0·0228	1′·12	0′·79
For a rise of 1 in Wolfer’s frequency	—	+0·0014	+0′·069	+0′·048

A grouping of the 11 years 1890 to 1900, according to Wolfer’s sunspot frequency, gave +0′·043 as the equivalent in declination range at Kew—whether from ordinary or quiet days—to 1 in Wolfer’s scale. We cannot hope to obtain more than rough approximations from 3 years near sunspot minimum, but it seems fairly clear that, so far as Wolfer’s figures and magnetic data are concerned, nothing abnormal was taking place.

* ‘Terrestrial Magnetism,’ vol. 29, p. 167.

§ 5. According to the above figures, if there is a linear relationship between the "solar constant" and sunspot frequency, then for a rise of 90 in Wolfer's scale—a rough average for the difference between sunspot maximum and minimum—we should expect a rise of over 0.12 in the "solar constant." If the values obtained for 1923 and 1924 are normal, we should thus expect the average values during the ensuing sunspot maximum years to be such as 2.05.

If we omit 1923, on the ground that Wolfer's figure for it is only provisional, we obtain 0.0019 as the equivalent on Abbot's scale of 1 on Wolfer's, and we have correspondingly enhanced expectations for the next sunspot maximum. If we take the figures from the three years 1921 to 1923, as above, and assume a linear relationship, we obtain as the equivalent to 0.01 in the "solar constant" scale 0'.49 in the Kew declination range on ordinary days, and 0'.35 in quiet days.

Another estimate was obtained from four successive 12-month periods, the first commencing with December 1920, the last ending with November, 1924. By contrasting the first two with the last two periods, 0'.57 was obtained as the equivalent in the Kew diurnal inequality declination range on ordinary days to 0.01 in the "solar constant" figure. In the course of an 11-year period we expect a rise of 4' or 5' in the Kew declination range between sunspot minimum and maximum. This again would suggest, on the basis of a linear relationship, values decidedly over 2.0 for the "solar constant" at sunspot maximum.

I have to thank the Director, Meteorological Office, for permission to use some still unpublished Kew magnetic data.

Some Further Experiments on the Gyromagnetic Effect.

By J. W. FISHER, B.Sc.

(Communicated by Professor O. W. Richardson, F.R.S.—Received 9 April, 1925.)

The experiments about to be described are of a similar nature to some preliminary ones described by the author on a previous occasion,* the idea underlying them being that a magnetizable substance, when magnetized by a rotating field in such a way that the magnetic elements or molecules of the substance rotate with the field, should, on the basis of the electron theory, develop a component of magnetization perpendicular to the plane in which the magnetizing field rotates, and in the direction in which a left-handed screw would progress when rotated in the same sense as the field according to the above theory. If Ω denotes the angular velocity of the rotating field, M and m the angular and magnetic moment respectively of the magnetic elements, the transverse component of magnetization should be given approximately by

$$I = \frac{M}{m} \Omega k,$$

k being the susceptibility of the material. (A deduction of this formula is given in the Appendix.)

In deriving this expression the quantity $J\Omega^2$, where J is the moment of inertia of an element through its centre of gravity and perpendicular to its magnetic axis, is neglected in comparison with M . Taking J to be of the order 10^{-40} and $M = h/2\pi = 10^{-27}$ approximately, corresponding to 1 Bohr magneton, and Ω of the order 10^5 , as in these experiments, we have

$$J\Omega^2/M = 10^{-3},$$

so that the above assumption appears justifiable. We arrive then at the above formula if we suppose that the magnetic molecules, or groups of molecules, rotate with the external field. If the field is too small it is conceivable that the molecules will not rotate with it and that, in consequence, there will be no effect. If this were not the case, it would follow from the formula that there would be an effect even for infinitely small fields, provided that K had a finite initial value. In order that an effect of the above kind may exist, it is by no means necessary that the elementary magnetic systems should revolve uniformly with the external field; indeed, in view of the intermolecular fields and mutual interaction of the systems, this would be

* 'Proc. Phys. Soc.,' vol. 34, Part V (Aug., 1922).

most improbable, except in the case of very strong fields. It would suffice if the elementary magnetic axes completed one revolution in the same period as the external field, the motion taking place perhaps by jumps between positions of unstable and stable equilibrium, the mean angular velocity being equal to that of the magnetizing field.

On the other hand, if the magnetizing field is not strong enough the axes may, during a part of the cycle, revolve in the same direction as the field, and then subsequently return to their initial positions, the total angular displacement being zero for one revolution of the field and thus giving rise to no effect, since the mean angular velocity is now zero. This is what might be expected to occur on the basis of Honda and Okûbo's theory* of ferromagnetic crystals, in which the couple on each magnetic molecule due to the magnetizing field is supposed balanced by that due to the neighbouring molecules. In this case it is easy to show that the molecules would not revolve with the magnetizing field unless the latter exceeds a certain value depending on the grouping of the molecules in the lattice.

In the special case of a cubic lattice it follows from Hondo and Okûbo's calculations that an induced intensity of magnetization of about one-fifth that corresponding to saturation would be necessary for such a rotation to occur; for all fields smaller than that corresponding to this intensity of magnetization the axes of the magnetic molecules would only oscillate backwards and forwards as the magnetizing field revolved. Under these circumstances it is, of course, not possible to predict a definite numerical value for the effect, or even to predict definitely a qualitative effect at all, owing to the uncertainty of the molecular rotations with the field; on the other hand, an effect of the kind is well worth looking for, since, in the event of its being established qualitatively and its dependence on the strength and frequency of the magnetizing field investigated, considerable light might be thrown on the theory of ferromagnetic crystals. Unfortunately no such effect has so far been observed, even with the strongest rotating fields which could be produced by the apparatus used, namely, 100-110 gauss.

Before proceeding with a description of the experiments it would seem desirable to point out the analogy between these experiments and those of S. J. Barnett,† in which he was able to detect the magnetization of an iron bar produced by rotation of the bar as a whole. The only difference between the two cases is that, whereas in Barnett's experiments the magnetic axes of the

* 'Science Reports, Tokohu Univ.,' vol. 5, p. 153 (1916).

† Barnett, 'Phys. Rev.,' vol. 6, p. 270 (1915).

molecules were caused to revolve by rotating the bar as a whole, in this case it was sought to produce such a rotation, at a much greater speed than would have been possible by the former method, by means of a high-frequency rotating magnetic field. The phenomena in the present case are consequently more complicated than in Barnett's experiments, owing both to the presence of the rotating field and also to the varying mutual actions of the magnetic molecules on one another during their individual rotations, if such occur. Apart from the possibility of the absence of the effect being accounted for by the non-rotation of the molecules with the magnetizing field, its absence might be accounted for from the standpoint of the quantum theory, but until more conclusive evidence regarding the possible non-rotation of the molecules has been obtained, it seems hardly worth while developing a theory along these lines. According to accurate measurements of the Richardson* and Barnett† effects, particularly the former, it appears that the ratio M/m has, very approximately, one-half the value $2m/e$.‡ This magneto-mechanical anomaly appears to be due, according to the theory of the anomalous Zeeman effect, to the central parts of the atom, and may perhaps be accounted for by supposing the nucleus itself to be quantized and to contribute to the mechanical moment of the "atomic core" without influencing appreciably its magnetic moment. Such an explanation of the magneto-mechanical anomaly has been put forward by Richardson§ and Braunbeck|| on the hypothesis that the atomic nuclei possess a quantized angular momentum in a sense opposite to that of the rotating electrons responsible for the magnetic moment, but the possibility of its accounting for the double value of the ratio m/M , which appears to hold for the "atomic core" in the case of the multiplets examined by Landé,¶ does not seem to have been pointed out.

If this is to explain the half value in the theory of Barnett's effect, it must imply a more or less rigid coupling between electrons and nucleus, for, in Barnett's experiments, the couple can be considered to be made up of two parts, one on the electrons and one on the nucleus, and, if the angular momenta are oppositely directed in the two cases, these couples will have opposite signs. For a weak coupling between electrons and nucleus these oppositely-directed couples should produce a displacement between the axes of rotation of electrons

* Chattock and Bates, 'Phil. Trans.,' A, vol. 223, p. 257 (1922).

† Barnett, 'Phys. Rev.' (2), vol. 6, p. 239 (1915); vol. 10, p. 7 (1917).

‡ W. Sucksmith, 'Roy. Soc. Proc.,' A, vol. 104, pp. 499-511 (1923).

§ Richardson, 'Roy. Soc. Proc.,' A, vol. 102, p. 538 (1922).

|| Braunbeck, 'Phys. Zeitschr.,' vol. 23, pp. 307-309 (1922).

¶ Landé, 'Zeitschr. f. Physik,' vol. 11, p. 353 (1922); vol. 19, p. 122 (1923),

and nucleus, and since the magnetic moment of the nucleus must be negligible in comparison with that of the electrons, the induced transverse magnetization parallel to the axis of rotation would have very nearly the full value predicted by the original theory ; if, on the other hand, the coupling is strong so that the whole system resembles a rigid whole, then the effect would be reduced to one-half of the former value as required, provided the absolute magnitude of the angular momentum of the nucleus is half that associated with the external electrons. These considerations do not apply so definitely to the Richardson effect, where only the relation between two steady states before and after magnetization comes into account. A possible explanation of such a rigid coupling between electrons and nucleus might perhaps be found in the theory of spacial quantizing, assuming the angular momentum of the nucleus to be quantized in the same way as that of the outer electrons. This question is, however, closely connected with the anomalous Zeeman effect, the quantum mechanics of which has not yet been satisfactorily elucidated.

The same considerations as apply to Barnett's experiments may be expected to apply also to the present case. The majority of the present experiments were made on magnetite, and it was thought that the absence of an effect might, perhaps, be explained by supposing the magnetic molecule to have no resultant angular momentum, for reasons similar to the above. In order to investigate this, Mr. Sucksmith kindly tested samples of the magnetite in his latest apparatus, and was able to show that the Richardson effect existed also in this case, and, at any rate to a close approximation, had, as in the other cases investigated, one-half the value given by the original formula. This being the case, the above-mentioned possibility of explaining the non-appearance of the effect is ruled out. The following experiments were carried out, using rotating fields of radio frequency, in which case the effect, if present, should be easily capable of detection, since it should be proportional to the angular velocity with which the field rotates. This makes it possible to use much more compact apparatus and ferro-magnetic substances of relatively low susceptibility.

Experimental Arrangements.

Owing to the high frequencies employed in these experiments, it is necessary to avoid the production of eddy currents, which might prevent the magnetizing field from penetrating the specimen ; the material must therefore have a low electrical conductivity. The material originally chosen for the experiments was magnetite from the Tilly Foster Mine, New York. Since with the first apparatus used the specimen had to be of cylindrical form and of fairly large

dimensions, the material had to be powdered, the compressed powder being contained in glass tubes. Besides possessing a relatively high permeability for magnetite, this substance combines low electrical conductivity with small retentivity, and would appear, therefore, to be particularly suitable. The magnetic field in the interior of the substance itself will be considerably smaller than the external field on account of the demagnetizing effect of the free surfaces. In the case of the powder the internal field can be estimated only approximately, owing to the irregular form of the particles of which it is composed.

Let H denote the external rotating field and $\bar{I}$ the magnetization produced in the powder as a whole. Further, let I be the actual magnetization in the substance, k its susceptibility, N and V the number per unit volume and the volume respectively of the powder particles. The transverse intensity of magnetization in each particle due to the effect in question is given by $2\frac{m}{e}\Omega k$, or half this if $M/m = m/e$, so that the average transverse magnetization in the powder would be :

$$2\frac{m}{e}\Omega KNV = 2\frac{m}{e}\Omega k\phi,$$

where ϕ denotes the actual volume of magnetite in unit volume of powder. The value of k here would be that corresponding to the particular magnetizing field in the interior of the particles. k may be estimated by determining experimentally the value of $\bar{I}$, and finding I from $\bar{I} = \phi I$, from which k may be obtained, using the known magnetization curve for the solid magnetite. By using a powder of sufficiently fine particles it is possible in this way to avoid the shielding effect of eddy currents and to experiment also with good conductors, such as iron, etc.

The rotating field was produced by two linear oscillating fields at right angles to one another, and differing in phase by $\pi/2$. The oscillating currents were maintained by means of thermionic valves designed to work on a low plate voltage. The accompanying diagram, fig. 1, shows the arrangement of the circuits and the method of securing the necessary phase difference between the two fields. The two oscillatory circuits are A_1, L_1, C_1 and A_2, L_2, C_2 , and the necessary reactance was obtained by inductive coupling between the oscillatory and grid circuits. The oscillatory circuit of one of the valves was coupled with the grid circuit of the other by coupling P_1 with G_2 . These coils were wound in the form of a variometer, one revolving inside the other, so that the coupling could be varied over a considerable range. The condensers C_3, C_4 across the mains were each of one-third microfarad capacity. In the

On continuing to distune the circuits, by varying the capacity, say, of one in the same sense as before, the same phenomena recur, and when the limit of the so-called "silent interval" is reached, free oscillations once more set in and beats occur with practically the same frequency with which they previously ceased. This phenomenon has been described by Appelton under the title of "Automatic Synchronization of Triode Oscillators" for the case of a strong oscillator coupled with a weak one,* and the method of adapting it to the present purpose and producing a magnetic field rotating with wireless frequencies was suggested to me by Prof. Richardson. The present method of coupling, in which the oscillatory circuit of one of the valves is coupled with the grid circuit of the other, was chosen because in this case the phase difference when automatic synchronization sets in is $\pi/2$, and this changes gradually, as the silent interval is traversed, to zero, corresponding to exact tuning ($L_1 C_1 = L_2 C_2$), and then to $-\pi/2$. It is therefore possible, by winding the two inductances $L_1 L_2$ as magnetizing coils at right angles to one another, to produce a magnetic field, the direction of revolution of which can be changed uniformly from one direction to the opposite one, by simply altering the capacity in one of the circuits by means of a variable condenser in parallel with the fixed capacity.

The condensers $C_1 C_2$ were standard plug-in condensers, and were usually set to 0.05 microfarad. In parallel with C_1 was a variable condenser, oil-filled, of about 0.002 mfd. capacity, and the direction of rotation of the field was changed by turning the vanes of this condenser between the extreme positions of synchronization. Hot-wire ammeters were inserted in each of the oscillating circuits, and, with the original apparatus, the currents registered varied from 0.25 to 0.5 amps. (R.M.S.), the corresponding field strengths at the axis of the magnetizing coils $L_1 L_2$ being 2-5 gauss. The strength of the rotating field is, of course, found by multiplying these values by $\sqrt{2}$. The accompanying diagram (fig. 2), shows the arrangement of the coils and specimen in the apparatus originally constructed.

The magnetizing coils $L_1 L_2$ were wound on rectangular ebonite frames 6.3 cms. long and 3.7 cms. wide, each set of four coils being connected in series. These coils had each 70 turns of No. 26 D.C.C. wire, and on the outside of each was wound a coil consisting of 100 turns of No. 35 D.C.C. wire, these four windings being likewise connected in series and to the grid circuit of the valve, thus providing the necessary grid coupling. Care of course had to be taken that each of these coils was wound in the right direction. The ebonite bobbins supporting

* Appelton, 'Trans. Camb. Phil. Soc.,' vol. 21, Part 3 (1922).

the coils L_1 L_2 were fixed to a rigid wooden frame provided with levelling screws. Along the axis of the coils was fixed a thick ebonite tube, e , in the interior of which the specimens contained in glass tubes could be inserted.

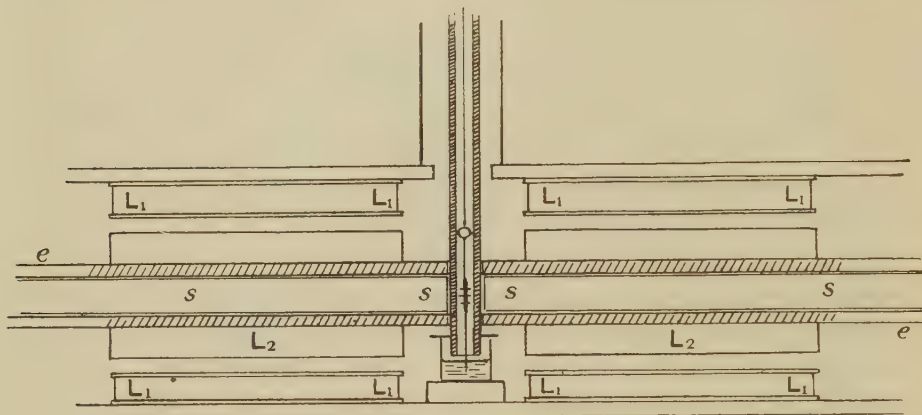


Fig. 2.

In order to detect the transverse magnetization looked for (*i.e.*, magnetization along the axis of the tube), a magnetometer was employed. This consisted of three small needles about 2.5 mms. in length passing through a thin ebonite strip attached to the end of a fine glass fibre, which carried at its upper end a small mirror. The whole was suspended, by means of a fine silk fibre, in a thick copper tube passing diametrically through the ebonite tube. This copper tube was some 30 cms. long, with an external diameter of 8.57 mms. and a thickness of 1.78 mms.; it was provided with a small glass window opposite the magnetometer mirror. The object of the copper tube was to shield the magnetometer needles from the direct action of the rotating field, for there might conceivably be a couple on the needles in the rotating field due to induced eddy currents, and this couple, although acting principally about a vertical axis, might cause a deflection of the needle and so give rise to spurious effects. For this reason metal was avoided wherever possible in the magnetometer and glass and ebonite used instead. No iron whatever was used in this apparatus apart from the magnetometer needles, since the state of magnetization of any iron so used might vary in the oscillating field through demagnetization, etc., and so cause variations of the steady field.

Superposed on the oscillating current in each circuit is a direct current, the mean value of which is equal to the plate current, and this, of course, gives rise to a permanent magnetic field, with an axial component arising from asymmetry in the coils, and which may moreover vary slightly when the

capacity in one of the circuits is altered in order to reverse the direction of rotation of the field. It was, therefore, necessary to arrange two neutralizing coils connected in series with their respective plate circuits, in the neighbourhood of the magnetometer needle, and to adjust the positions of these so that no permanent deflection could be observed when the plate currents were switched on. This adjustment had to be made with the specimen in position. The plate currents were of the order of 30 milliamperes and, without these compensating coils, caused deflections of several centimetres. It is also of great importance to ensure that no direct current shall flow in the grid coils, since such currents, although small, might cause large deflections on account of the large number of turns in these circuits. In order to make it impossible for such currents to occur, grid condensers were inserted, the grids being of course provided with suitable grid leaks to the filaments. In this way any permanent deflection on switching on either of the valves was eliminated, and, moreover, no change in the mean position of the spot could be observed when the oscillators were synchronized and the direction of rotation of the field reversed without the specimen present.

The frame with the magnetizing coils and magnetometer was supported on a bracket cemented into a thick wall, but even then the spot moved continually on account of vibratory disturbances. The lower end of the copper tube was finally removed and a small dash pot fitted filled with oil, into which dipped a fine glass rod attached to the lower end of the ebonite strip carrying the magnetometer needles. This had the desired effect of reducing the disturbances considerably without impairing the sensitivity. The finely powdered magnetite was contained in two glass tubes each 13 cms. long and 9.65 cms. internal diameter, and placed so as to butt up against the copper tube enclosing the magnetometer, the width of the gap being then about 11.5 mms. These could be easily inserted or withdrawn as required. The field strength at the axis due to a known current in the coils was measured and found to be about 8.1 gauss per ampere. Naturally the field along the axis will be far from uniform, but this can hardly be avoided without introducing other difficulties, and again since the effect should depend on the susceptibility and not directly on the field strength, this should not matter very much.

The method of securing the necessary phase difference of $\pi/2$ has already been described, and it was seen that the rotating field of constant intensity occurs only in the limiting positions of the condenser vanes, *i.e.*, at the points where automatic synchronization sets in and ceases respectively. Very precise

adjustment of the variable condenser is, therefore, necessary, and in order to make this possible an oscillograph had to be used.

The oscillograph employed was of the cathode-ray type made by the Western Electric Company. This is made to operate on a voltage of 250–300 volts, and has an oxide-coated filament as emitting cathode. Sharp focussing of the spot on the fluorescent screen is brought about by the ionization of the residual gas in the tube, and the sensitivity is such that a deflection of about 1 mm. is produced by a potential difference of 1 volt across one pair of deflecting plates. Two small air core transformers were used, the primaries consisting of a few turns of thick copper wire connected in series with the oscillating circuits. The secondaries, which could be slid in or out over the primaries, were connected each to one pair of deflecting plates, so that the phase relation between the currents in the two circuits could be seen at a glance from the pattern on the fluorescent screen, and the size of this pattern, which changed, of course, with the frequency of the oscillations, could be adjusted by varying the coupling between primary and secondary of the transformers. By this means the phases could be adjusted with great precision, the circles corresponding to the rotating field of constant amplitude being very good, provided the frequency was not too large. By just exceeding the limits of the "silent interval" the circles disappeared and were replaced by a fuzzy pattern due to the free oscillations setting in. When this occurred the note corresponding to the beat frequency was usually distinctly audible, and appeared to originate from the vibrations of the wires carrying the alternating currents in the earth's field.

In order to form an estimate of the magnitude of the effect to be expected it becomes necessary, as already mentioned, to determine the magnetization of the specimen in the rotating field, and this can be calculated approximately if the average magnetization $\bar{I}$ in the powder is known; it will be convenient to regard the powder as a homogeneous substance of susceptibility $\bar{k}$. The magnitude of the external field being H , we have

$$\bar{I} = \bar{k}H/(1 + 2\pi\bar{k})$$

since the specimen is cylindrical and magnetized in a direction perpendicular to its axis. Differences in the value of $\bar{k}$ might be expected to arise from small differences in the compression of the powder in various tests. On filling a tube, however, with the magnetite and compressing the latter by tapping the tube on a table a stage was always reached when a loud metallic click resulted from each tap, and when this occurred the powder appeared to be quite firm and to admit of no more compression. This procedure was adopted

in every case, also when filling the tubes for the actual experiments. The value of $\bar{k}$ may be determined by several methods. The value obtained for $\bar{k}$ for steady fields using the magnetometer method was 0.24, and it was found to be constant over a large range of fields. In order to determine $\bar{k}$ directly for the rotating field under the actual conditions of the experiment two different methods were employed. In the first of these the couple on a small brass cylinder, hung in the rotating field, was measured, first with the cylinder suspended freely in the field, and then with it surrounded by a hollow cylinder of magnetite. The susceptibility may be deduced, as described below, from the ratio of the couples in the two cases. A second and more direct method is to measure the induced alternating e.m.f. in a small coil, first without the magnetite present, and then with the coil imbedded in the powder. The vacuum thermo-junction necessary for this was not available when the first of these methods was worked out.

The apparatus was arranged vertically, and the ebonite tube e was removed and replaced by two glass tubes arranged concentrically. The annular space between the two tubes could be packed with magnetite. In the interior of the inner tube a small brass cylinder was suspended along the axis; this consisted of a brass rod 2 cms. long and 2 mms. diameter. The suspension was of fine phosphor bronze, and the permanent deflection due to the eddy currents in the cylinder, when the field was caused to rotate, could be read off by a mirror and scale. The outside tube had an internal diameter of 0.992 cms., while the external diameter of the inner tube was 0.582 cms., thus leaving an annular gap of width 0.205 cms. which could be filled with magnetite. The magnitude of the rotating field was kept as nearly constant as possible by observing the circle on the oscillograph screen, and the couples measured with and without the magnetite present. The values of k can then be deduced as follows. In the first place it will be clear that, since the couple on the conducting cylinder is due entirely to the interaction between the rotating field and the eddy currents induced by it, the magnitude of the couple will vary as the square of the rotating field, and, consequently, the square root of the ratio of the deflection without the magnetite to that with the magnetite present will be equal to the ratio of the original rotating field H to the field H' which it produces in the interior of the hollow cylinder of magnetite of the above dimensions. If, moreover, we assume that the angle of lag between the external field H and the induced magnetization in the magnetite is small, we can treat the problem as a static one in evaluating H' in terms of H , $\bar{k}$ and the radii of the cylinder of magnetite.

Suppose the external field H uniform and let a , b denote respectively the external and internal radii. Let ϕ_1 ϕ_2 ϕ_3 be the potentials characterizing the field (a) at points outside the cylinder; (b) in the magnetite; (c) in the interior of the hollow cylinder. It is easy to see that the potential must be of the form $\phi = (Ar + B/r) \cos \theta$, using polar co-ordinates, the angle being measured from the direction of the external field H . In order to satisfy the boundary conditions we must have :

$$\phi_1 = \left(-Hr + \frac{B_1}{r} \right) \cos \theta; \quad \phi_2 = \left(A_2 r + \frac{B_2}{r} \right) \cos \theta; \quad \phi_3 = -H'r \cos \theta$$

where

$$\begin{aligned} B_1 &= \frac{(a^2 - b^2) \psi}{\psi^2 - b^2/a^2} H; & B_2 &= \frac{-b^2 (\psi - 1)}{\psi^2 - b^2/a^2} H; \\ A_2 &= \frac{\psi (\psi - 1)}{\psi^2 - b^2/a^2} H; & H' &= \left(1 - \frac{1 - b^2/a^2}{\psi^2 - b^2/a^2} \right) H; \\ \psi &= \frac{\bar{\mu} + 1}{\bar{\mu} - 1} = 1 + \frac{1}{2\pi \bar{k}}. \end{aligned}$$

This result is, of course, valid only when the cylinder is sufficiently long in comparison with its diameter for us to be able to treat the problem as one in two dimensions. In the present case, however, where the ratio of length to diameter was about 15, the above should represent very approximately the actual conditions. With a rotating field of strength 4 gauss the mean deflection measured without the magnetite present was 16.5 cms., while that with the magnetite was 7.8 cms. from which it follows, by substitution in the above formulæ, that $\psi = 1.57 = 1 + \frac{1}{2\pi \bar{k}}$ or $\bar{k} = 0.28$ approx. This will be the value of $\bar{k}$ corresponding to the field in the magnetite powder, and this is found from the potential ϕ_2 . Using the above value for ψ , this field varies from a maximum of $0.69 H = 2.8$ gauss to a minimum of $0.15 H = 0.6$ gauss. Thus for this range of fields $\bar{k}$ has the approximate value 0.28 which is in good agreement with the values deduced from measurements with the second method. In this case the value of $\bar{I}$ may be determined directly in terms of the external field H . The ratio x of the e.m.f. induced in the coil when imbedded in the magnetite to that with it in air will give the ratio of the magnetic inductions $\bar{B}$ to the field H , and, since the material is cylindrical, we have

$$\bar{B} = xH = H + 2\pi \bar{I}; \quad \bar{I} = \frac{x-1}{2\pi} H.$$

The alternating current induced in a small coil 2 cm. long and 3 mm. wide, consisting of 10 turns of fine wire, was measured by means of a vacuum thermo-junction in connection with a sensitive galvanometer, with and without the magnetite present. The apparatus had to be previously calibrated by small known direct currents. The susceptibility $\bar{k}$ deduced in this manner agreed very well with that found by the former method.

In order to estimate the angle, if any, between the induced magnetization and the rotating field a small glass bulb, filled with powdered magnetite, was suspended in the rotating field and the couple on it found by observing the deflection as in the previous experiment. If $\bar{I}$ denotes the magnetization and V the volume of the globe the couple will be given by :

$$C = \bar{I}VH \sin \psi,$$

where ψ denotes the lag between $\bar{I}$ and H . The values of C for various known values of H (calculated from the known oscillating currents) could be deduced from the scale deflections, the couple per unit angle of twist being found from the period and moment of inertia of the globe. The volume of the bulb was 0.57 c.c. and contained 1.255 gms. of magnetite so that the density of the powder was 2.15 as compared with 4.1 in the solid state. For values of H ranging from 1.7 to 5.2 gauss the value of ψ was as nearly as possible constant and equal to 1.6° , this value being obtained by taking $\bar{k} = 0.28$. Taking $H = 4$ gauss we find then $\bar{I} = 0.4$, and taking $\phi = \frac{1}{2}$ as a rough approximation we should have $I = \bar{I}/\phi = 0.88$ approx., and it is seen from the magnetization curve for the solid magnetite that this value of I corresponds to a susceptibility k of approximately 0.6, which value may be used in estimating the magnitude of the possible effect. The ratio of I to $I_{\max.}$ is very small; $I_{\max.} \approx 3 \cdot 10^2$.

The frequency of the oscillations was determined by a resonance method. A circuit was set up in the vicinity of the oscillatory circuits, consisting of a standard plug-in condenser in parallel with a known inductance, calculated from Nagaoka's Tables, and a crystal detector operating a galvanometer. The inductance in the resonance circuit was calculated to be $1.05 \cdot 10^{-4}$ henries, and, using condensers of 0.05 microfarad in the oscillating circuits, the resonance capacity was 0.085 mfd., from which the frequency works out to :

$$n = 5.341 \cdot 10^4; \quad \Omega = 2\pi n = 3.29 \cdot 10^5.$$

In order to determine the direction of rotation of the field a light aluminium cylinder, provided with a small mirror, was stretched horizontally in a glass tube between phosphor bronze strips, and this glass tube could be inserted in the

ebonite tube. The direction of rotation of the field was found at once from the direction in which the cylinder tended to rotate under the action of the induced eddy currents.

In order to be able to form some estimate of the magnitude of the effect to be expected, it is necessary first of all to calculate the field at the magnetometer needle produced by a given intensity of magnetization parallel to the axis of the specimen. This can, of course, be calculated only approximately on account of the non-uniform and unknown distribution of magnetization in the specimen. We can, however, arrive at an approximate value by considering the field to arise from two equal distributions of surface density I over the ends of the magnetite cylinders forming the gap in which the needle is suspended. Thus, denoting by a the radius of each cylinder (internal rad. of containing tube) and the width of the gap by $2b$, we have for the field F at a point on the axis midway between the faces :

$$F = 4\pi I \left(1 - \frac{b}{\sqrt{a^2 + b^2}} \right).$$

In the present case b was 5.75 mms. ; $a = 4.83$ mms. giving :

$$F \approx 2.9 I.$$

The sensitivity of the magnetometer was determined and it was found that a field of 10^{-4} gauss at the needle caused a scale deflection of 2.3 mms. If the value of k be taken as 0.6 and $\phi = 0.5$, then the value for the expected transverse intensity of magnetization I' gives :

$$I' = 2 \frac{m}{e} \Omega k \phi = 2.5 \cdot 7 \cdot 10^{-8} \cdot 3 \cdot 29 \cdot 10^5 \cdot 0.28 \cdot 0.5 = 5.2 \cdot 10^{-3}.$$

Since the change in the transverse intensity on reversing the direction of rotation of the field is twice this, the change in the field at the magnetometer should be given by

$$\Delta H \approx 3 \cdot 10^{-2} \text{ gauss,}$$

which, on the above estimate, should cause a deflection of

$$3 \cdot 10^{-2} \cdot 10^4 \cdot 2.3 = 690 \text{ mms.}$$

In no case, however, could a deflection of even 1 mm. be detected, so that, even allowing for the somewhat rough approximations made in estimating the magnitude of the effect to be expected, it seems certain that no effect of the kind was present in these experiments.

The intensity of magnetization in the magnetite, as computed above, is seen to be very small, and, as already mentioned, it is possible that under such

circumstances no general rotation of the elementary magnetic systems would occur. It appeared therefore very desirable to repeat the experiments, using the strongest rotating fields obtainable with the given oscillators. In order to obtain strong fields, irrespective of the frequency, it is necessary in the first place to increase as much as possible the number of turns in the magnetizing coils, and at the same time to reduce the dimensions of these as much as possible. In addition, the capacities and grid coupling have to be chosen to produce the maximum oscillatory currents.

A new apparatus was accordingly constructed based on a somewhat modified design. This time only two coils at right angles were used as magnetizing coils, the specimens being contained in a glass tube passing through the centre of these coils. The glass tube passed through a hole drilled along the axis of a rectangular ebonite block, of square cross-section, with side 1 cm. and length 6 cms. This block was provided on its four sides parallel to the axis with flanges in which the magnetizing coils L_1 , L_2 were wound. These coils were wound on first, and then on the outside of each were wound the coils M_1 , M_2 connected to the grid circuits. It was therefore impossible to bring the magnetometer needle close to the end of the specimen, on account of the coils. Accordingly the magnetic circuit was extended by two iron armatures, each consisting of a bundle of fire iron wires, and the magnetometer needle, shielded as in the previous case by the copper tube, was placed at one end of the iron armature. Each of the magnetizing coils consisted of 400 turns of No. 34 D.S.C. copper wire, and the two coupling coils consisted each of 500 turns of the same wire. The completed bobbin had an external diameter of about 6 cms. and an overall length of 14 cms. On account of the asymmetry due to the overlapping of the magnetizing and grid coils, the mutual coupling between the two circuits is somewhat complicated and the circles obtained on synchronization were not so good as in the former case. The field at the centre of a rectangular coil of sides $2a$, $2b$ is given by

$$H = \frac{4\pi i}{10} \frac{\sqrt{a^2 + b^2}}{ab}$$

where n is the number of turns and i the current in amperes. In this case the mean values of a and b were 1.2 and 3.3 cms. respectively, so that the field at the centre works out at approximately $140 i$ gauss. A large accumulator battery became available at this time, and by using the mains in series with a portion of this the plate voltage on the valves was increased to about 400 volts. The maximum currents in the oscillating circuits were obtained for capacities of 0.05 microfarad, the R.M.S. value being about 0.5 amps. The current ampli-

tude being in this case 0.71 amperes, the corresponding magnetic field at the centre of the coils works out at about 100 gauss, or about 25 times that obtainable with the original apparatus. The total length of the magnetite specimen used in this case was 4.3 cms., and it will be seen from the graph, fig. 3, that the variation of the axial field over this distance is about 13 per cent. only, and, moreover, the minimum value of 100 gauss occurs at the centre of the coil.

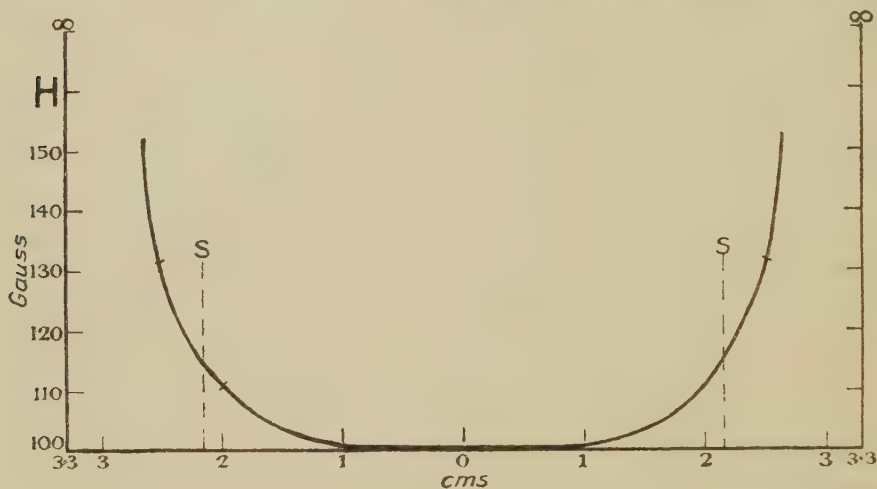


Fig. 3.

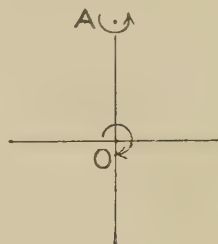
It is improbable that fields much in excess of this could be produced with the oscillators used, since there is clearly a lower limit to the size which the bobbin and specimen can have (the sensitivity being proportional to the cross-section of the latter), and there is also a limit to the size and number of turns, both on account of the good insulation necessary between oscillatory and grid coils and the current-carrying capacity of the windings. The exterior of the bobbin became very warm after a run of a quarter of an hour or so. The internal diameter of the tube containing the specimen was 5 mms., and it had a length of 15 cms. The frequency was now reduced to about a half of its former value on account of the increased inductance, and when in operation the apparatus emitted a shrill, piercing note, caused apparently by vibrations of the wires carrying the oscillating currents in the earth's field, as the effect was enhanced in the presence of a strong magnet. Also, the beat note between the two frequencies was distinctly audible as a low musical note, and helped considerably in tuning the circuits. The mutual coupling between the circuits had to be greatly increased in this case. The frequency was determined as before by means of a circuit tuned to resonance; using the same fixed inductance

as before ($1.05 \cdot 10^{-5}$ henries) the resonance capacity was 0.45 mfd. with 0.5 mfd. capacity in the circuits, the corresponding frequency being

$$n = 2.3 \cdot 10^4; \quad \Omega = 1.45 \cdot 10^5.$$

In this case it was not so easy to obtain good circles on the oscillograph screen in the limiting positions of synchronization, and matters were made worse by the fact that after running for a time the valves got much softer, on account of the overloading necessary to get large oscillating currents. The direction of rotation of the magnetic field could be determined at any instant by the direction in which a light aluminium cylinder suspended horizontally at A, just above one of the magnetizing coils, tended to rotate.

It is easy to see that if the direction of rotation of the field at the centre of the coils is, say, clockwise, then at a point just above one of the coils, as at A, the direction of rotation will be opposite, or anti-clockwise. This small cylinder was provided with a mirror and reflected a beam of light on to a vertical scale fixed



by the side of the magnetometer scale, so that the instantaneous direction of rotation of the field at the centre of the bobbin could be found at once from the position of the spot on this scale. The presence of the iron core between the magnetite specimen and the magnetometer caused in the first instance considerable disturbance. A large part of this was due to the magnetization of the iron wires by the direct current to the plates of the valves, and it was therefore necessary to separate the direct component from the alternating currents. This was accomplished without appreciable loss in alternating-current amplitude by inserting condensers of one-third microfarad capacity in series with the oscillating circuits, and providing a path for the direct-current component through iron-cored choke-coils between the high-tension source and the plates. This improved matters considerably, but there remained still certain amount of disturbance due to the iron. Most of this was successfully got rid of by enclosing the bundle of iron wires forming the core in a thin copper tube extending over the whole of their length, and thus shielding them from the non-uniform fields at the ends of the bobbin, where the windings overlapped. Since the steady current component through the magnetizing coils was now removed, the compensating coils were no longer necessary.

A deflection was always observed when the field was changed from a rotating field in one direction to a linear oscillating one, *i.e.*, on passing through half the silent interval; the spot returned, however, nearly to its original position

on completing the cycle, so that there was no great difference in the positions of the spot with the field rotating in opposite directions. Whatever the cause of this disturbance, its effect is therefore nearly eliminated by taking the change of deflection, if any, corresponding to the two opposite directions of rotation of the field. In addition to the sample of magnetite used in the previous experiments, tests were also made with finely powdered artificial magnetic iron oxide, and also with very finely divided iron powder; the concluding tests were made using a sample of the solid magnetite ground down to a cylindrical rod to fit in the glass tube. The induced magnetization in the powders was determined in each case by measuring the alternating current induced in a small rectangular coil of two turns embedded in the substance. The values found for $\bar{k}$ in each case did not differ greatly; the values for Tilly Foster magnetite, artificial magnetite, and finely divided iron powder were 0.25, 0.13, and 0.22 respectively.

The method cannot, however, be considered very accurate. The magnetometer required very careful adjustment in this case owing to the close proximity of the iron core; the sensitivity was such that a scale deflection of 1 cm. resulted from a field of $3.5 \cdot 10^{-4}$ gauss. Considerable increase in sensitivity was obtained by using an astatic pair, and, after the rough adjustments had been made, the sensitivity was increased as much as possible by adjusting the current flowing in a small coil clipped on to the copper tube containing the magnetometer opposite the upper needles of the astatic pair. The field at the needle due to an intensity of magnetization I in the specimen was calculated to be $0.85 I$, assuming no leakage of magnetic lines of force over the surface of the iron core. The amount of such leakage is difficult to estimate, but it could hardly be sufficient to alter the order of magnitude of the calculated field. The deflection to be expected on reversal of the field, taking $\phi = 0.5$ as before, would be about 25 cms. (or half this if $M/m = m/e$), whereas in every case the change of deflection did not exceed a few millimetres, and, if such a change was observed, it was always in the opposite sense to that deduced from the theory. Negative results were also obtained with artificial magnetite and iron powder.

On account of the high frequency and the good conductivity of iron it is necessary that the individual particles should be extremely fine in order that the field may penetrate them. If the particles be considered as spheres of radius a the condition to be satisfied is that

$$4\pi^2 \lambda \mu n a^2 \ll 1 *$$

* Gans, 'Archiv f. Elektrotechnik,' vol. 9, p. 413 (1921).

where λ denotes the conductivity, μ the permeability, and n the frequency. Substituting the appropriate numerical values we find $a \ll 3 \cdot 10^{-3}$ cms. taking $\mu = 10^3$, a value certainly much in excess of the actual value for the small internal field. In order to obtain particles sufficiently fine, the iron powder had to be obtained by reducing the oxide at a bright red heat in a current of hydrogen. By this means a powder having particles of $0.5 \cdot 10^{-2}$ to $1 \cdot 10^{-3}$ cms. radius was produced, and, as a further guard against eddy currents in the mass, the powder was first soaked in oil.

Taking the intensity of magnetization in the iron to be about 25 (with $\phi = 2.3/7$, *i.e.*, the ratio of density of powder to that of solid iron) the susceptibility should be much greater than in the case of magnetite, for it has been shown that even up to frequencies higher than those used here the susceptibility of iron for rotating fields does not vary much from its value for steady fields.* In this case also no effect could be detected. The final observations were made, as already mentioned, on a solid specimen of the original magnetite, ground down to a cylinder 4.3 cms. long and 4 mms. diameter. The rotating field would penetrate such a cylinder without appreciable loss on account of the extremely low conductivity, and moreover the theoretical effect to be expected would be greater than in the case of a powder on account of the much greater density. (The value of k calculated for this case for a rotating field of 100 gauss is 1.14, giving $I/I_{\max.} \approx 1/20$.)

As in the previous cases the results were entirely negative, the small deflections, amounting to a few millimetres, which were usually observed when the direction of rotation of the field was reversed, being always in the opposite sense to that indicated by the theory, and must be attributed to some other cause of disturbance. Observations were made more difficult by the irregular motion of the spot, which occurred in spite of the damping, and in addition there was a slow drift in one direction, due apparently to the gradual demagnetization of the iron core under the action of the oscillating field. By taking a number of consecutive observations corresponding to successive reversals of the field, it was found that there was no appreciable difference between the mean change of deflection observed without the magnetite specimen present and that observed with it:

Considering the large value of the effect to be expected from theory it may be concluded that no effect of the kind under consideration is present under the conditions of these experiments. Its absence might be attributed, apart from other reasons, to the non-rotation of the magnetic elements with the

* Tonks, 'Phys. Rev.', February, 1924.

field, an hypothesis which might perhaps be tested by experiments using still stronger rotating magnetic fields. An ideal substance from this point of view would, of course, be a paramagnetic gas, or even liquid, but unfortunately the volume susceptibility in all such cases would be too small to cause effects large enough to be detected magnetically.

In conclusion I wish to express my grateful thanks to Prof. Richardson for the interest he has taken in these experiments and for much helpful advice. I also wish to thank Prof. Ernest Wilson, for the loan of magnetite and apparatus.

Summary.

Experiments are described in which it was sought to detect a gyromagnetic effect by magnetizing a substance (in most cases magnetite) by a rotating magnetic field, and looking for a component of magnetization in a direction perpendicular to the plane of rotation of the field; such a component would be expected to arise if a rotation of the magnetic axes of the molecules is set up by the rotating field. Fields rotating at frequencies of $2-5 \cdot 10^4$ cycles per second were produced by valve generators, but no evidence of an effect of this kind was found, even for rotating fields of over 100 gauss. The magnitude of the effect to be expected has been calculated, and the sensitivity of the apparatus was such that it should have been easily capable of detection if present.

APPENDIX.

Let x, y, z be a fixed co-ordinate system (for simplicity omitted from the

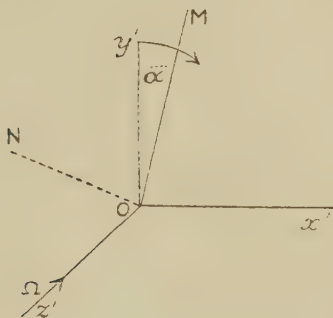


diagram) and x', y', z' a system rotating with the field H (with angular velocity Ω), the z and z' axes being coincident. Let the magnetic axis OM of the atomic system be situated in the $y'oz'$ plane, and let it make an angle α with the y' axis. Let A, B, C be the moments of inertia about OM , the x' axis, and an axis ON in the $y'oz'$ plane perpendicular to OM , respectively. Denoting differentiation with respect to the time in the rotating system by d'/dt , we have :

$$\frac{dM_0}{dt} = \frac{d'M_0}{dt} + [\Omega, M_0], \quad (1)$$

where M_0 is the resultant angular momentum, determined by the vector equation

$$M_0 = (\overline{M + A \Omega \sin \alpha}) - \overline{C \Omega \cos \alpha}. \quad (2)$$

M is the angular momentum about OM due to the electron rotations, and we write

$$M = 2 \frac{m}{e} m, \quad (3)$$

where m denotes the magnetic moment. If G denotes the couple exerted on the elementary magnet by the field H , we have

$$G = \frac{dM_0}{dt} = [H, m], \quad (4)$$

and by (1)

$$\begin{aligned} \frac{d'M}{dt} = G' &= [H, m] - [\Omega, M] - [\Omega, A \Omega \sin \alpha] + [\Omega, C \Omega \cos \alpha], \\ &= \left[H - 2 \frac{m}{e} \Omega, m \right] + \overline{(A - C) \Omega^2 \cos \alpha \sin \alpha}. \end{aligned}$$

The last vector on the right-hand side is perpendicular to the $y'oz'$ plane; we neglect it since $(A - C) \Omega^2/M$ is small. The equivalent field in the rotating system is thus $H - 2 \frac{m}{e} \Omega$; since Ω and H are at right angles to one another, this field will be directed in the $y'oz'$ plane and will make an angle ϕ with H , such that $\phi = \tan^{-1} \left(2 \frac{m}{e} \cdot \frac{\Omega}{H} \right)$. The direction of this equivalent field should determine the direction of magnetization in the rotating system of co-ordinates. Since ϕ is small, the transverse component of magnetisation (parallel to oz') thus set up would be, approximately,

$$I_z = 2 \frac{m}{e} \cdot \frac{\Omega}{H} I = 2 \frac{m}{e} \Omega k \left(\text{or half this if } M = \frac{m}{e} m \right),$$

where k is the susceptibility of the substance. As already mentioned, this result is valid only if an individual rotation of the atomic axes is produced by the field; in the case of an irregular, but general rotation of the axes in one direction, we should expect an effect of the same order of magnitude as that given by the above formula.

The Composition of Soap Films.

By MARY EVELYN LAING.

(Communicated by Prof. J. W. McBain, F.R.S.—Received April 14, 1925.)

In a recent article on "The Investigation of Properties of Thin Films by X-rays," Sir William Bragg discusses the nature and composition of soap films and the black spots that form therein. He proceeded from the assumption that "the ordinary thick film is bounded on one side by a molecular film of oleic acid," such acid being formed by the "hydrolysis of the sodium or potassium oleate in solution."

The brief experimental investigation outlined below, carried out with solutions of sodium oleate whose degree of hydrolysis is known, shows that free oleic acid does not exist in soap films, but sodium soap is stored in the surface of a soap solution or soap bubble.

Almost all physical studies of soap films have been undertaken in a reactive atmosphere, namely, one containing oxygen and carbon dioxide, without thought as to its effect upon the sensitive film. Apart from the rapid and complicated oxidation that occurs, there is appreciable interaction between the carbonic acid and soap. The extent to which soap is decomposed through formation of carbonate is subject to the usual principle of mass action, and it is well known to the technical chemist that, under suitable conditions, the replacement of fatty radicle by carbonic acid may be made extensive. Hence, on the chemical side, the results obtained by such investigators as Perrin and Milner have to be accepted with reserve. For example, Milner produced foam by bubbling ordinary air through solutions of sodium oleate, and measured the change in electrical resistance, ascribing it to the removal of the soap films. Again Perrin succeeded in completely decomposing sodium oleate by prolonged blowing through it, converting it to oleic acid.

Under normal conditions carbon dioxide reacts only to a certain extent with soap solution, forming, not free fatty acid, but solid acid sodium soap, which usually remains in colloidal suspension. Sodium carbonate is, however, much more hydrolysed than soap, and is sometimes used in place of sodium hydroxide in the manufacture on a large scale. The crystalline sediments which often appear in dilute solutions of soluble soaps are found on analysis to consist of hydrated acid sodium salts, each equivalent of acid usually being combined

with several equivalents of neutral soap.* The term acid soap was introduced by Chevreul, but it does not represent a definite compound which can be prepared in pure condition, but rather an isomorphous mixture or sorption compound whose composition depends upon conditions.†

All the experiments on soap bubbles here recorded were carried out in an inert atmosphere of pure nitrogen, so that the surface films should not be chemically altered.

Experimental.

Three methods of examination were adopted, namely, electrical conductivity, refractive index and complete chemical analysis. The materials used were the purest obtainable, and the soap solutions were prepared, as previously described, from sodium drippings and Kahlbaum's best oleic acid (mol. wt. 282.5) with boiled-out conductivity water. The concentration of every original soap solution used was obtained by direct analysis. Varying weights of soap were decomposed with known amounts of hydrochloric acid (Hulett and Bonner, 1909, 31, 390), and the oleic acid separated by filtration through a wet filter paper. The oleic acid was titrated direct with alcoholic soda, and the filtrate titrated for total sodium. The analyses recorded are the mean results of several concordant analyses.

Changes in concentration were also measured in the conductivity experiments by means of the Zeiss interferometer, reading to eight significant figures, original solutions being taken in every case for comparison. Concentrations are expressed in weight normality. The conductivity measurements were carried out and corrected in the same careful manner as in previous measurements, a cell of borosilicate glass of low cell constant and an accurate 10-metre bridge being used. All instruments and vessels were calibrated before use.

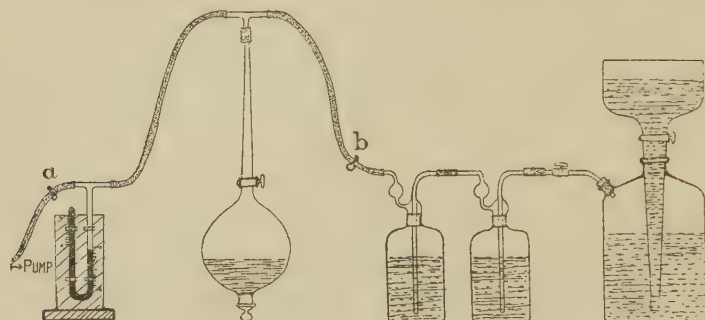
Apparatus and Outline of Experiment.

The apparatus consisted of a large litre separating funnel which was connected on one side through a manometer to a pressure pump and on the other through wash-bottles to an aspirator containing nitrogen. About 150 c.c. of soap solution are placed in the separating funnel which is inverted. Clip *b* is closed and *a* is opened and the funnel evacuated until the solution froths; *a* is then closed and *b* opened and nitrogen, from which any trace of air is

* In the extreme dilutions used by du Nouy (less than N/1,000,000, 'Phil. Mag.,' 1924, vol. 48, p. 664) hydrolysis is certainly complete, but it should be remembered that all the fatty acids are very much stronger than carbonic.

† See footnote p. 621, McBain, Taylor and Laing, 'J.C.S.,' vol. 121 (1922).

removed, is passed in. When bubbling ceases *b* is again closed, and the process repeated. This procedure is carried out three times, the flask being



left finally full of pure nitrogen; *a* and *b* and the funnel tap are closed. The funnel is then thoroughly shaken and placed upright, and the liquid allowed to settle for two minutes, when it is quickly run into a Jena bottle. A large bulk of liquid (about 100 c.c.) drains and collects in this time, and is termed the residue. Liquid again settles out by froth collapsing, and this is tapped off into another Jena bottle and termed "intermediate solution." The firm foam which now fills the flask, and has apparently no loose liquid clinging to it, is allowed to stand overnight in the dark. The condensed foam generally occupies about 25 c.c. As the foam from any one separation did not give rise to sufficient solution for chemical analyses in duplicate, duplicates were obtained from samples of foam from separate experiments. When the soap of the same concentration was treated under comparable conditions of time, temperature, etc., the agreement was complete.

Table I.—Specific Conductivity Measurements of Original Soap Residues and Foam.

Normality of original soap.	Original soap.	Specific residue.	Conductivity.		Per cent. diff. increase.
			Per cent. diff.	Foam.	
0.05153	0.001127	0.001088	3.5	0.001166	+ 3.5
0.04561	0.001051	0.001027	2.3	0.001092	+ 3.9
0.04561	0.001051	0.001042	0.9	0.001075	+ 2.3
0.04953	0.001124	0.001104	1.8	0.001150	+ 2.2
0.04953	0.001124	0.001091	2.9	0.001147	+ 2.1
0.04953	0.00124	0.001105	1.7	0.001132	+ 0.9
Mean			2.2	—	+ 2.5

Tables I and II give the result for the examination of the specific conductivity and of the refractive index. The percentage change in refractive index is calculated as change in amount of soap although this cannot be strictly accurate.

Table II.—Concentration Changes in Residue and Foam as Measured by Zeiss Interferometer.

Normality of soap.	Concentration of residue.	Per cent. diff.	Concentration of foam.	Per cent. increase.
0·05153	0·05076	1·6	0·05230	+ 1·5
0·04561	0·04508	1·2	0·04678	+ 2·6
0·04561	0·04556	0·23	0·04492	+ 1·5
0·04953	0·04235	0·36	0·05118	+ 3·3
0·04953	0·04934	0·39	0·05303	+ 7·1
0·04953	0·04937	0·33	0·05034	+ 1·6

Table III illustrates the data obtained in duplicate experiments by the final method of direct chemical analysis, and all the final results obtained from the means of such duplicates are collected in Table IV.

Table III.—Results of Chemical Analyses of Original Solution of Sodium Oleate and the Foam obtained therefrom.

Experiment.	Original.		Foam.	
	As Na.	As fatty acid.	As Na.	As fatty acid.
1	0·04943	0·04749	0·05277	0·05076
2	0·04927	0·04746	0·05353	0·05069
3	0·04989	0·04764	—	—
Mean	0·04953	0·04753	0·05265	0·05072
	Per cent. increase		6·3	6·7

Here the accumulations of sodium and fatty acid are nearly equivalent corresponding to nearly neutral soap.

Table IV.—Complete Chemical Analyses of Solutions of Sodium Oleate and the Foams derived therefrom.

Original.	Residue.	Intermediate.	Per cent. increase.	Foam.	Per cent. increase.
Na.* 0.05012	0.04890	—	—	0.05136	2.47
Fa. 0.05012	0.04837	—	—	0.05262	4.34
Na. 0.05012	0.04952	—	—	0.05140	2.55
Fa. 0.05012	0.04902	—	—	0.05194	3.63
Na. 0.05012	—	—	—	0.05177	3.29
Fa. 0.05012	—	—	—	0.05295	5.65
Na. 0.04943	—	—	—	0.05277	6.76
Fa. 0.04749	—	—	—	0.05075	6.84
Na. 0.04927	—	—	—	0.05253	6.61
Fa. 0.04746	—	—	—	0.05069	6.86
Na. 0.05117	0.03556	0.05425	6.02	0.05488	7.25
Fa. 0.05222	0.05154	0.05426	3.91	0.05835	11.74
Na. 0.04973	0.04961	0.05007	1.97	0.05913	18.90
Fa. 0.05261	0.05200	(0.05246)	—	0.06552	24.51
Na. 0.04973	0.04826	0.05960	19.82	0.06116	22.46
Fa. 0.05261	0.04093	0.06874	30.64	0.07023	33.49
Na. 0.04663	0.04528	0.04871	4.46	0.05926	26.86
Fa. 0.04183	0.04061	0.04448	5.68	(0.05218)	24.75

* In the tables "Na." indicates analysis for total sodium; "Fa." total fatty radicle measured in the form of oleic acid. Concentrations are expressed in weight normality.

Table V.—The Composition of the Material which accumulates in Foam from N/20 Sodium Oleate with additions of Oleic Acid or Alkali.

Equivalents per cent. added.	Per cent. increase Na.	Per cent. increase Fa.	Ratio.	Composition.
Nil (neutral)	2.77	4.54	0.61	NaOl + 0.61 HOl
2.1 acid	7.25	11.74	0.62	NaOl + 0.62 HOl
5.8 acid	20.68	34.00	0.61	NaOl + 0.61 HOl
4.2 alkali	6.68	6.84	0.98	NaOl
11.5 alkali	15.66*	15.21*	1.03	NaOl

* Mean of columns 4 and 6, Table IV; bubbles extremely unstable, whereas all others were very stable.

Discussion.

It will be noticed that in every case the foam gains in concentration at the expense of the bulk of the liquid (residue).

It will be seen from Table I that the condensed foam has gained and the

residue has lost in specific conductivity. Taking these two facts together, we arrive at some indication of the type of substance which has accumulated at the surface. An increase in concentration might have been due to oleic acid itself; but if soap had been replaced by oleic acid the specific conductivity would have been diminished. Further, if oleic acid were formed by hydrolysis and removed by the surface film, the residue should have greatly gained in conductivity due to the alkali set free. The mean values of all experiments show that what is lost in conducting material from the residue is gained in the foam, which is compatible with the accumulation only of some sort of salt in the foam.

Finally, the direct analytical data summarised in Table V show clearly that an acid sodium soap collects in the surface, and not oleic acid as such. The composition of the material in the surface is NaOleate. 0.61Holeic. An excess of alkali in the solution suffices to transform the material adsorbed in the surface into neutral sodium oleate.

It should be noticed, too, that the absolute amount of substance adsorbed differs according to the nature of the investigated solution. It is least in neutral solution, increasing with addition of either oleic acid or alkali.

Previous work on N/20 solutions of sodium oleate has shown that it is largely composed of crystalloid, one-half being in the form of simple sodium oleate (NaOl), and one-fifth simple oleate-ion (Ol'), in addition to one-twentieth ionic micelle, one-eighth neutral micelle and 2.8 per cent. acid soap formed by hydrolysis. Accumulation of this crystalloidal soap will be strongly opposed by osmotic and possibly electrical forces, and adsorption is at a minimum. It will be seen that only 2.8 per cent. of the total sodium was taken into soap films from these neutral crystalloidal solutions.

Addition of acid forms further acid soap, whilst addition of alkali drives back the dissociation of the colloidal electrolyte. In both cases, since colloid is formed we should expect its accumulation on the surface, since it is unopposed by osmotic or electric forces.* Referring to our Table V we find that a soap containing 6 per cent. excess acid gains 21 per cent. in concentration in the foam, and a soap containing 11 per cent. excess alkali gains 15 per cent. soap, which is much greater than the $2\frac{1}{2}$ per cent. for neutral soap solution. The same effect of the addition of small quantities of either acid or alkali was observed by studying the carbon number of soaps.†

* It is interesting to recall that an aqueous suspension of the almost completely insoluble acid sodium palmitate of the empirical composition NaP. HP froths excellently.

† McBain, Harbourn and King, 'J. Soc. Chem. Ind.,' vol. 42, p. 373 T. (1922).

This conclusion is supported by experiments by Griffin ('J.A.C.S.', 1923, vol. 45, p. 1648) on emulsions of mineral oil with soap and water. Emulsions of kerosene with solutions of sodium oleate were allowed to cream, and the amount of soap going into the interface determined by analysis. Griffin, like ourselves, found that more fatty acid than alkali metal was removed from the solution, unless the soap contained alkali in excess to prevent hydrolysis, in which case alkali and fatty acid were removed in equivalent amounts. On the assumption that oleate was present in the film as a monomolecular layer, Griffin found the thickness $44 \text{ \AA.U.}$, which compares favourably with De Broglie's 46 for oleate curd. This value comes nearest that found by Wells, namely, $43 \text{ \AA.U.}$ as minimum thickness of the black film; whereas the thickness of a double oleic acid film according to Shearer is 36. All these data agree well with the conclusion that the structural basis of the black spot of soap films is an acid sodium soap. The soap and acid sodium soaps in the film are certainly hydrated, but this has been found not to affect the molecular spacing appreciably. It is easy to conceive of the formation of black films from sodium soap and acid sodium soap, which are known to form large structures such as colloidal particles, crystals and crystallites.

The surface of the solution affords the mechanism for building the continuous layer, and the black spot results when two such films come into contact through the soap solution receding. This is very like drops or bubbles of saponin solution, where solid surface films do not shrink smoothly but wrinkle and shrivel when the volume is diminished. On the other hand, it is difficult to conceive of stable formation of a sheet of pure liquid, such as oleic acid, since the black spot exhibits a surface tension as great as that of an ordinary soap film, and almost the whole of this free energy would be liberated through the oleic acid shrinking to a sphere.

Summary.

Direct analysis of the material accumulated in soap films shows that it is not free fatty acid, but an acid sodium soap of the composition $\text{NaOlO} \cdot 61\text{HOl}$. This result is in accordance with Sir William Bragg's recent suggestion that the black spot in soap films is due to the actual contact of the two adsorbed layers, except that it consists of acid sodium soap, probably hydrated, instead of free fatty acid. The stability of soap films is much more readily understood if they are made of this colloidal material rather than of a pure liquid such as oleic acid.

Structure in the Secondary Hydrogen Spectrum.—II.

By O. W. RICHARDSON, F.R.S., Yarrow Research Professor of the Royal Society.

(Received June 17, 1925.)

This paper continues the reduction of this spectrum into groups of related lines, starting from the lines which are selectively weakened in electron discharges, in hydrogen at low pressures, of the types already described.*

Table I.—Series No. 159 R.

Properties.							Wave-length in Air.	Wave- number.	1st Diff.	2nd Diff.	3rd Diff.
(1)	(2)	(3)	(4)	(5)	(6)	(7)					
+		—	+				6161·59	I, II 16225·11 (7)			
++		++		Z			6021·23	I, III 16603·19 (7)	378·08		
++		++	+				5916·24	I, II 16897·97 (6)*	294·78	83·30	1·01
								III, 156 Q (6)	210·47	84·31	1·36
							5843·45	17108·44 (0)		85·67	
									124·80		0·77
			++	++			5801·14	17233·24 (3)		86·44	
			++	+			5788·25	157 Q (5)	38·36		0·76
								17271·60 (4)		87·20	
			++	++			5804·66	17222·76 (1)	— 48·84	87·23	0·03
			—				5850·89	17086·69 (2)	—136·07		—0·51
			++				5928·20	156 Q (5)	—222·79	86·72	
								16863·90 (2)			
								Missing			1·24
											=3×0·41
										265·40	
										=3×88·47	
			+				6186·52	16159·71 (0)			
							6379·24	15671·52 (0)	—488·19		

Unresolved doublet (M and B). I, II, and III denoted weakened in first, second, and third type discharges respectively. 156 Q (6), etc., denote lines which are also claimed by the alternative arrangements so designated. These ions are used throughout in similar tables.

The series designated 159 R and shown in Table I is unusually long, but the properties and the numerical values of the wave-numbers look convincing.

* Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 106, p. 640 (1924).

The intensities are a bit irregular, but on the whole fall off steadily from $m = 1$ to $m = 12$. Two lines which are not known to be doublets are claimed by alternative series as 156 Q (5) and 157 Q (5). The second differences show a regular increase to a maximum, at any rate from $m = 1$ to $m = 7$, and the third differences show a steady diminution. There are two sets of lines which might be associated with 159 R as Q series. These are shown in Table II. It is difficult to distinguish between the claims of these alternative Q series, as the remaining lines of these Q series and most of the lines of the associated P series, if they exist, would lie in the unexplored part of the spectrum beyond Merton and Barratt's red limit. If 159 Q is the Q series corresponding to 159 R, there is a line 15390.36(0) ..., ..., ..., +, ..., ..., ..., wave-length in air 6495.78, which gives the following combination :

$$159 \text{ Q } (2) + 159 \text{ Q } (3) \text{ (Table II)} = 159 \text{ R } (2) \text{ (Table 1)} + 15390.36 + 0.72.$$

If this is 159 P (3) the lowest values of m for which lines occur would be R (1) Q (2) and P (3). The strength and regularity of the intensities of the lines, the fact that two of them are enhanced in the condensed discharge and the increment in the 3rd difference make 159 Q' (m) look more probable than 159 Q

Table II.—Series No. 159 Q (m).

m .	Properties.							Wave-length in Air.	Wave-number (Int.).	1st Diff.	2nd Diff.	3rd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)					
2								6241.18	16018.20 (2)			
3								6257.63	15976.07 (0)	42.13	80.55	
4								6306.06	15853.39 (0)	122.68	80.35	-0.20
5								6387.87	15650.36 (1)	203.03		

Series No. 159 Q' (m).

1			+					6329.60	†15794.41 (6)			
2								6362.48	15712.79 (5)	81.62	81.66	
3								6429.30	15549.51 (3)	163.28	82.66	+1.00
4			+			F ?		6532.62	15303.57 (1)	295.94		

† Absent at -252° C. (MacLennan and Shrum*).

* Trans. R.S. Canada, 3rd Series, vol. 18, p. 177 (1924).

(m) as a Q series for 159 R (m). If there is a P series showing combinations with 159 Q' (m) and 159 R (m) P (1) and P (2) do not exist (unless 15287·07 (2) and a weak diffuse line 15279·5 are a split-up of P (2), which is unlikely, particularly as 15287·07 has been claimed as a Fulcher line) and the lines of higher quantum number all lie in the unknown region beyond the red limit.

The values of the term differences, on the alternative assumptions that 159 Q and 159 Q' respectively are associated with 159 R, are shown in Table III.

Table III.—Initial term differences assuming 159 R and 159 Q are associated.

$$F(m+1) - F(m) = R(m) - Q(m)$$

$$\begin{array}{rcll} F(3) - F(2) = R(2) - Q(2) = & 584\cdot99 & \begin{array}{l} \nearrow 336\cdot91 \\ \searrow 333\cdot15 \end{array} & \begin{array}{l} \\ \end{array} \\ F(4) - F(3) = R(3) - Q(3) = & 921\cdot90 & & -3\cdot76 \\ F(5) - F(4) = R(4) - Q(4) = & 1,255\cdot05 & \nearrow 327\cdot83 & \\ F(6) - F(5) = R(5) - Q(5) = & 1,582\cdot88 & & -5\cdot32 \end{array}$$

Final term differences assuming 159 R and 159 Q are associated.

$$f(m+1) - f(m) = R(m) - Q(m+1)$$

$$\begin{array}{rcll} f(2) - f(1) = R(1) - Q(2) = & 206\cdot91 & \begin{array}{l} \nearrow 420\cdot21 \\ \searrow 417\cdot46 \end{array} & \begin{array}{l} \\ \end{array} \\ f(3) - f(2) = R(2) - Q(3) = & 627\cdot12 & & -2\cdot75 \\ f(4) - f(3) = R(3) - Q(4) = & 1,044\cdot58 & \nearrow 413\cdot50 & \\ f(5) - f(4) = R(4) - Q(5) = & 1,458\cdot08 & & -3\cdot96 \end{array}$$

Initial term differences assuming 159 R and 159 Q' are associated.

$$\begin{array}{rcll} F(2) - F(1) = R(1) - Q(1) = & 430\cdot70 & \begin{array}{l} \nearrow 459\cdot70 \\ \searrow 458\cdot06 \end{array} & \begin{array}{l} \\ \end{array} \\ F(3) - F(2) = R(2) - Q(2) = & 890\cdot40 & & -1\cdot64 \\ F(4) - F(3) = R(3) - Q(3) = & 1,348\cdot46 & \nearrow 456\cdot41 & \\ F(5) - F(4) = R(4) - Q(4) = & 1,804\cdot87 & & -1\cdot65 \end{array}$$

Final term differences assuming 159 R and 159 Q' are associated.

$$\begin{array}{rcll} f(2) - f(1) = R(1) - Q(2) = & 512\cdot32 & \begin{array}{l} \nearrow 541\cdot36 \\ \searrow 540\cdot72 \end{array} & \begin{array}{l} \\ \end{array} \\ f(3) - f(2) = R(2) - Q(3) = & 1,053\cdot68 & & -0\cdot64 \\ f(4) - f(3) = R(3) - Q(4) = & 1,594\cdot40 & & \end{array}$$

On the whole the association with 159 Q' seems the more consistent. If this association is real, the initial moment of inertia is very close to the final moment of inertia for 83 R (m),* which has the lowest values, both initial and final, for any series hitherto published; the final moment of inertia would be close

* Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 107, p. 602 (1925).

to the very small initial value for 83 R (m) but apparently somewhat lower. If the association is with 159 Q, the initial moment of inertia is similar to the initial moment of inertia for 3 P (m)* and a number of others, and the final moment of inertia to the corresponding quantity for 53 P (m)* and of Fulcher's second band. In any event the moment of inertia must be quite low, and the intensity distribution in either series is consistent with low values of the moments of inertia, the maximum intensity in the series under consideration being at or about $m = 1$.

If in the combination 159 R 159 Q we put $B = 168.46$ from $F(3) - F(2) = B(5-2P) = 584.99$ we obtain $P = 0.764$ and putting $b = 210.10$ from $f(2) - f(1) = b(3-2\rho) = 206.91$ we obtain $\rho = 1.0075$. These values of P and ρ are equal respectively to $\frac{3}{4}$ and 1 to within the degree of accuracy to which B and b are determinable from the data. Putting $P = \frac{3}{4}$ and $\rho = 1$ and taking the same values of B and b we obtain from $F(m) = B(m-P)^2$, $F(1) = 10.53$, $F(2) = 263.22$, and $F(3) = 852.83$. Similarly from $f(m) = b(m-\rho)^2$ $f(1) = 0$ and $f(2) = f(2) - f(1) = 206.91$. From these values both the equations $\nu_0 = Q(2) - F(2) + f(2) = R(1) - F(2) + f(1)$ give $\nu_0 = 15961.89$.

If the combination is 159 R 159 Q' we have by proceeding similarly and taking $B = 230$ and $b = 271$ $P = 0.564$ and $\rho = 0.554$. Thus, to a first approximation these term numbers are of the half-quantum type. However, the approximation $P = \rho = \frac{1}{2}$ does not appear to be good enough for the data, so we put $F(1) = 230(1 - 0.564)^2 = 43.70$, whence, using $F(2) - F(1) = 430.70$, $F(2) = 474.40$. Similarly using $\rho = 0.554$ $f(1) = 53.93$ and $f(2) = 566.25$; with these data both the equations $\nu_0 = Q(1) - F(1) + f(1) = R(1) - F(2) + f(1)$ give $\nu_0 = 15804.64$.

In the series in Table IV, the line 17355.21 is marked II ? because it is not absolutely clear from a re-inspection of the plates whether the line which is weakened here is this line or 17357.80 (4) +, ..., ++, ..., ..., ..., and in fact both these lines are probably weakened. The lines 17047.13 (5) and 17355.21 are marked III ? because this part of the spectrum is so weakened generally in the 3rd type discharge that it is difficult to say whether there is any selective weakening or not. The first line is claimed by another series as 153 P (2).

The second differences on Merton and Barratt's measurements of five of the lines and Tanaka's measurement of the other are so irregular that at first I was inclined to abandon this series. However, in order to arrive at a decision

* Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 107, p. 602 (1925).

Table IV.—Series 152 R.

<i>m</i> .	Properties.							Wave-number (Int.) (M and B, or T).	1st Diff.	2nd Diff.	Wave- number (Williams).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)						
1	++		+	++	Z			I, II, III 153 (2) *16710·70 (8)			16710·60		
2	++		++					III ? 17047·13 (5)	336·43	28·35	17047·16	336·56	28·67
3	+		++	O				I, II ? III ? 17355·21 (4)	308·08	29·49	17355·05	307·89	28·85
4			+					17633·80 (0)	278·59	28·39	17634·09	279·04	29·13
5								17884·00 (<i>q</i>)	250·20	29·41	17884·00	249·91	29·15
6			+					†18104·79 (0)	220·79		18104·76	220·76	

I, II, III denote weakened in 1st, 2nd, and 3rd type discharges respectively.

* Weakened at -252°C .† Absent at -252°C . (McL. & S.).

on the matter I asked Mr. W. E. Williams to re-measure these lines along with a few others in the same region, thrown in so as to spoil the series, relatively to one another. The results of Mr. Williams's re-measurements are given in the last three columns of Table IV, from which it would appear that the irregularities in the second differences are no greater than the errors of measurement. Mr. Williams found the faint line 17884·00 particularly difficult to measure with accuracy, and he is of the opinion that the assigned value might be 0·05 too low, in which case the two last second differences would be changed from 29·13 to 29·08 and from 29·15 to 29·25, giving the practically constant successive third differences of 0·18, 0·23 and 0·17 cm. In view of this regularity on re-measurement, it seems improbable that the series is a coincidence. Up to the present I have not noticed any other series which are connected with it, so that the enumeration is not really determined. The assigned values of m seem, however, pretty probable. In any event, the moment of inertia must be similar to that assigned to the sources of Fulcher's 1st Band, and the distribution of intensity among the lines is consistent with such a value of the moment of inertia. If this series is represented by $R(m) = \nu_0 + Ce(2m - 1) + Cd m^2$ the constants, determined from the first three lines, are $\nu_0 = 16535\cdot40$, $Ca = 175\cdot30$, $Ce = 189\cdot48$, $Cd = -14\cdot17_5$. If it is represented by $R'(m) = \nu_0 + \frac{1}{4}Cd + (Ca + Ce)m + Cd m^2$, the constants become $\nu_0 = 16349\cdot47$, $Ca = 182\cdot39$, $Ce = 196\cdot57$ and $Ca - Ce = Cd = -14\cdot17_5$. The last value of Ca ,

viz., 182.39, is very close to the value of Ce (183.24) got from 10 P (*m*) and to a value of the initial B (183 to 184) given by the band 84 PQR dealt with below.

Table V.—Series 185 P.

<i>m.</i>	Properties.							Wave-length in air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
2								4994.11	20018.02 (1)		
3								5069.73	19719.43 (1)	298.59	15.65
4	++			++				5143.53	83 R (2) II	282.94	14.48
5				++				5215.57	II	268.46	18.41
6?								5284.50	*19168.03 (1)	250.05	
									18917.98 (4)		

Series 185 Q.

1		++						4878.10	20494.07 (1)		
2		++						4874.28	20510.13 (1)	16.06	14.40
3								4867.05 41	59 Q (1) Q (2) I, II, III	30.46	14.02
4				O				4856.54	I, II, III	44.48	15.40
5								4842.45	20585.07 (5)	59.88	16.60
6?	++			O				4824.58	20644.95 (1)	76.48	
									20721.43 (2)		

Series 185 R.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
1		++			O		S	4763.82	20985.70 (4)	344.85	14.55
2		++						4686.79	21330.55 (2)	359.40	13.97
3								4609.14	21689.95 (<i>p</i>)	373.37	13.68
4		++						4531.14	22063.32 (0)	387.05	16.80
5				++			S	4453.02	II, III	403.85	
6?								4374.34	22450.37 (1)		
									22854.22 (<i>r</i>)		

I, II, III denote weakened in 1st, 2nd, and 3rd type respectively.

* Absent at -252°C . (McL. and S.).

The series in Table V give combinations leading to the differences and term numbers shown in Tables VI and VII.

Table VI.—Initial Terms of 185 P.Q.R.

m .	$R(m) - Q(m)$.	$Q(m+1) - P(m+1)$.	Diff.	Means.	Term Diff.	2nd Diff.
1	491.63	492.11	- 0.48	491.87	$F(2) - F(1)$	328.92
2	820.42	821.16	- 0.74	820.79	$F(3) - F(2)$	
3	1,149.36	1,148.58	+ 0.78	1,148.97	$F(4) - F(3)$	328.18
4	1,478.25	1,476.92	+ 1.33	1,477.59	$F(5) - F(4)$	328.62
5	1,805.42	?? 1,803.45	+ 1.97	1,804.44	$F(6) - F(5)$	328.50*
6?	2,132.79	—	—	2,132.79	$F(7) - F(6)$	327.37*

* Term involving P (6) disregarded in computing these numbers. I, II, III denote weakened in first, second, and third type respectively.

Table VII.—Final Terms of 185 P.Q.R.

m .	$R(m) - Q(m+1)$.	$Q(m) - P(m+1)$.	Diff.	Means.	Term Diff.	2nd Diff.
1	475.57	476.05	- 0.48	475.81	$f(2) - f(1)$	314.52
2	789.96	790.70	- 0.74	790.33	$f(3) - f(2)$	
3	1,104.88	1,104.10	+ 0.78	1,104.49	$f(4) - f(3)$	314.16
4	1,418.37	1,417.04	+ 1.33	1,417.71	$f(5) - f(4)$	313.22
5?	1,728.94	?? 1,726.97	+ 1.97	1,727.96	$f(6) - f(5)$	311.23*

* Term involving P (6) disregarded in computing this number.

The terms, both initial and final, are of a very simple type and the second differences are nearly constant. In fact, for the initial terms the constant P in $F(m) = B(m - P)^2$ only differs from zero by about $\frac{1}{4}$ per cent., and the corresponding quantity ρ for the final terms only differs from zero by a little over 1 per cent. These deviations from zero, although in excess of observational errors, are probably not in excess of theoretical uncertainties implicit in any formula for the terms which does not extend to powers of m beyond the second.

If we assume provisionally that P and ρ each equal zero for this band, we obtain $F(1) = B = 164.28$ and $f(1) = b = 157.26$. From these the higher term numbers can be calculated from the data in Tables VI and VII. The successive values of ν_0 computed from

$$\nu_0 = P(2) - F(1) + f(2) = Q(1) - F(1) + f(1) = R(1) - F(2) + f()$$

are 20486·81, 20487·05 and 20486·81 with a mean value of 20486·89. It is very interesting to observe that both the initial and final moments of inertia for this band are practically identical with those which were assigned by Prof. Tanaka and myself to Series No. 3 P (*m*),* which lies in an entirely different part of the spectrum. The comparison is as follows :—

Series No. 3 P (*m*)—

$$Ca = 164\cdot11, \quad Ce = 156\cdot70, \quad Cd = +7\cdot41, \quad \nu_0 = 17086\cdot27.$$

Band No. 185 P (*m*), Q (*m*), R (*m*)—

$$B = 164\cdot28, \quad b = 157\cdot26, \quad B - b = +7\cdot02, \quad \nu_0 = 20486\cdot89.$$

The initial moment of inertia of the emitters of 185 PQR is also almost the same as the initial moment of inertia of 60 R (*m*) for which $Ca = 165\cdot07$, whilst the final moment of inertia of 185 PQR is almost the same as the initial moment of inertia for Fulcher's first band for which Ca is about 157, 27 P' (*m*) for which $Ca = 157\cdot36$, and the final value for 11 R' (*m*) for which $Ce = 157\cdot54$.

Some of the individual lines in this band require a little further consideration. 185 P (5) is marked II ? in Table V because it is not absolutely certain whether the weakened line is this line or 19171·45 (2) or both of them. It is fairly certain that P (6) is not 18917·98 (4) unless the line is abnormal, and this line has been disregarded in computing some of the data in Tables VI and VII. 185 P (4) is also claimed by 83 R (2) and 185 Q (3) by both 59 Q (1) and 41 Q (2). 19436·49 (3) seems too strong as 185 P (4), so that possibly it is a blend. 20450·59 (2) has been re-examined and is almost certainly not double. Its doubtful position in 59 Q (*m*) was referred to in dealing with that series. As regards 41 Q (2) five of the lines attributed to 41 Q (*m*) are already claimed by other and apparently better series, so that 41 Q (*m*) may have to be abandoned. The evidence strongly points to the view that 20540·59 is a single line and belongs only to the band 185 PQR. The line 20585·07 (5), which appears to be too strong as 185 Q (4), seems on the plates as though it might be double, with a faint component, intensity about 1, about 0·3 Å.U. on the long wave side of the main line ; so that most of the strength is still at or about 20585·07 (5). The line 20721·43 (2) is almost certainly single. The intensity distribution given by Merton and Barratt for the lines of this band is very irregular, only the R series showing an approximation to what would be expected from the moments of inertia. The distribution in the 2nd type discharge does, however, show some indication of an approach to a more normal distribution. *

* 'Roy. Soc. Proc.,' A, vol. 107, p. 613 (1925).

Table VIII.—Series 111 P (*m*).

<i>m</i> .	Properties.							Wave-length in air.		Wave number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)					
3					O			4505·63	I II III	22188·25 (3)		
4	++			++	O			4550·96	*Im III _m 11 R (6)	21967·16 (3)	221·09	38·28
5	+			+				4605·35	II _m S a Q (6)	21707·79 (0)	259·37	37·67
6	+							4669·25	11 R (5)	21410·75 (1)	297·04	

* Weakened at -252° C. (McL. and S.).Table IX.—Series 61 Q (*m*).

<i>m</i> .	Properties.							Wave-length in air.		Wave number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)					
1				++				4434·31		22525·06 (-)		
2				++	Z		S	4447·56	II _m III _m	22477·97 (4)	47·09	36·32
3				++				4464·12	I II	†22394·56 (1)	83·41	34·77
4	++			++	Z		S	4487·80	II III	*22276·38 (3)	118·18	36·21
5							S	4519·13		22121·99 (0)	154·39	

† Unresolved doublet (M. and B.).

* Absent at -252° C. (McL. and S.).Table X.—Series 204 R (*m*).

<i>m</i> .	Properties.							Wave-length in air.		Wave number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)					
1				++	Z		S	4417·32	112 Q (3)	22631·80 (3)		
2								4407·06	I, II, III	22684·53 (<i>r</i>)	52·73	34·60
3								4403·54		22702·66 (<i>g</i>)	18·13	29·93
4								4405·83		22690·86 (<i>r</i>)	-11·80	41·87
5				+				4416·27		22637·19 (1)	-53·67	

Although the band 111 P (m) 61 Q (m) 204 R (m) has elements of weakness, it has other features which help to make up for them. Every line of any strength is in the list of weakened lines prepared by Prof. Tanaka and the writer. The Q series looks quite convincing; it has the strength in the even and weakness in the odd quantum numbers which seems to be one of the very common features of Q series in this spectrum. The lines of the band are mostly high-pressure or helium lines. On the debit side we have to set some irregularities in the term numbers, which will be considered below, the unsatisfactory R series with the strength where the weakness ought to be and *vice versa*, and with the irregular second difference in the wave numbers and the fact that the P series does not give the Zeeman effect, but the other two branches do. Among minor matters P (4) = 21967·16 is claimed also by 11 R (6) and by Q (6) of Sandeman's* band and 21410·75 by 11 R (5). The credentials of 11 R (m) are altogether not very strong,† and 11 R (6) in particular is a very doubtful member of it. 21410·75 (1) may well be too strong both in 11 R (5) and in 111 R (6). 21967·16 is certainly required for Q (6) of Sandeman's series, but there seems to be room for both. This also applies to 22631·80, which is claimed both as 204 R (1) and 112 Q (3). I hope to be able to re-examine these lines at leisure later.

The usual operation of the combination principle on this band gives the results shown in Tables XI and XII.

Table XI.—Initial Terms of 111 P 61 Q 204 R.

m .	R (m) — Q (m)	Q ($m + 1$) — P ($m + 1$)	Diff.	Means.	Term Diff. 2nd Diff.
1	106·74			106·74	F (2) — F (1)
2	206·56	206·31	+ 0·25	206·44	F (3) — F (2)
3	308·10	309·22	— 1·12	308·66	F (4) — F (3)
4	414·48	414·20	+ 0·28	414·34	F (5) — F (4)
5	515·20			515·20	F (6) — F (5)

* Sandeman, 'Roy. Soc. Proc.,' A, vol. 108, p. 607 (1925).

† Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 107, p. 612 (1925).

Table XII.—Final Terms of 111 P 61 Q 204 R.

m .	$R(m) - Q(m+1)$	$Q(m) - P(m+1)$	Diff.	Means.	Term Diff. 2nd Diff.
1	153.83			153.83	$f(2) - f(1)$
2	289.97	289.72	+ 0.25	289.85	$f(3) - f(2)$
3	426.28	427.40	- 1.12	426.84	$f(4) - f(3)$
4	569.87	568.59	+ 0.28	568.73	$f(5) - f(4)$
5		711.24		711.24	$f(6) - f(5)$

The second differences of the term numbers are irregular; so that it is only possible to say that the initial B is about 50 and the final b about 68. These values are almost as low as those for 1 P 28 Q 102 R, and indicate high moments of inertia for both states. The intensity distributions in the P and Q series are not unreasonable for these values of B and b , but the R series is strong where it should be weak and *vice versa*. This fact and the irregular second differences in Table X throw some doubt on the reality of this R series. The series 111 P (m) and 61 Q (m) seem to stand on a stronger foundation.

Setting $B = 50$ and $b = 68$, we obtain $P = 0.44$, $F(1) = 15.68$, $F(2) = 122.42$ and $\rho = 0.37$ $f(1) = 26.99$ $f(2) = 180.82$ $f(3) = 470.67$. From these values of $F(m)$ and $f(m)$ we find by successive use of the equations $\nu_0 = P(3) - F(2) + f(3) = Q(1) - F(1) + f(1) = R(1) - F(2) + f(1)$ the value 22536.50, 22536.37 and 22536.37 for ν_0 .

The following Q series has practically the same second difference as the foregoing, so that it may be convenient to record it here. It has also a value of ν_0 not far from the one just obtained. The maximum strength is at the third member. This line is also claimed by 204R (1), which should, however, be a very faint line for its intensity to be reasonable in that series. (See Table XIII.)

The two alternatives for $m = 1$ may be the same line. 22545.11 (0) is a line measured by Merton and Barratt, and 22545.93 (0) is a line measured by Tanaka. The lines 22570.66 (0) and 22866.60 (p) are faint lines measured by Tanaka. No search has yet been made for other series associated with 112 Q (m). If 112 is a Q series, it fades away towards the violet in contrast to 61 Q (m).

The constants of 112 Q (m) cannot be fully determined until the associated series are known, but the values of $Q(2) - Q(1)$ and the second differences show that it deviates from the straightforward whole and half-quantum types. If we use $Q(m) = \nu_0 + F(m) - f(m)$ and put $F(m) = B(m - P)^2$ and

Table XIII.—Series 112 Q (m).

m .	Properties.							Wave-length in air.	Wave number (Int.).	1st Diff.	2nd Diff.
1	(1)	(2)	(3)	(4)	(5)	(6)	(7)	4434.31	22545.11 (0)	25.55	35.59
1								or 4434.15	22545.93 (0)	24.73	36.41
2								4429.29	22570.66 (0)	61.14	37.33
3				++	Z		S	4417.32	I, II, III 204 R (1)	98.47	37.86
4					Z			4398.19	I, II, III	136.33	
5								4371.97	22866.60 (p)		

$f(m) = b(m - \rho)^2$, we obtain from the second differences $2(B - b) = 37.20$ and from $Q(2) - Q(1)$, $2BP - 2b\rho = 31.07$. If P and ρ have the same sign, as they have in all the cases known at present, these equations cannot be satisfied with reasonable values of B and b unless both P and ρ are close to unity. In that case both $F(1)$ and $f(1)$ are small and the value of ν_0 is close to $Q(1)$.

The lines in Table XIV appear to form a whole quantum band. The intensities are somewhat irregular. 84 P (2), 84 Q (5), and 84 R (2) are also claimed as 53 P (4), 10 P (4), and 56 R (3) respectively. The line 21167.02 certainly has sufficient strength to fill both positions. The others are certainly required both in 53 P and 10 P. The credentials of 53 P as a series are better than those of 10 P. There is a line 20033.86 (1) ..., ++, —, +, ..., ..., which might be related to 84 P (m), but it has been assigned to 83 R (3).

Table XIV.—Series 84 P (m).

m .	Properties.							Wave-length in air.	Wave number (Int.).	1st Diff.	2nd Diff.
1	(1)	(2)	(3)	(4)	(5)	(6)	(7)	4989.26	20037.47 (p)	340.22	21.95
2								5075.44	II, 53 P (4)	318.27	21.48
3				—	—			5159.80	19378.98 (1)	296.79	
4		++	=					5239.04	19082.19 (2)		

Table XIV—*continued*.

<i>m.</i>	Properties.							Wave-length in air.	Wave number (Int.).	1st Diff.	2nd Diff.
Series 84 Q (<i>m</i>).											
1								4944·81	20217·58 (2)	29·21	22·10
2								‡4937·71	*20246·79 (<i>g</i>)		
3								4925·20	20298·10 (2)	51·31	19·68
4		++						4908·03	20369·09 (1)	70·99	19·19
5								4886·40	I, II, III, 10 P (4)	90·18	20·54
6								‡4860·10	20459·27 (1)	110·72	
									20569·99 (1)		
Series 84 R (<i>m</i>).											
1		+						4813·61	20768·64 (2)	398·38	20·14
2					Z			4723·01	II, III 56 R (3) §		
3					Z			4631·44	III	21585·54 (3)	20·33
4		++			Z			4539·15 <i>Im</i> , <i>IIIm</i> , <i>IIIIm</i>	22024·39 (2)	438·85	18·61
5								‡4446·80	†22481·85 (<i>g</i>)	457·46	

* The wave number of this line is taken as the mean of Tanaka's value 20246·69 and Williams' re-measurement 20246·89.

† The wave number of this line is taken as the mean of Tanaka's value 22481·81 and Williams' re-measurement 22481·89.

‡ Tanaka's measures.

§ Weakened at -252°C . (McL. and S.).

Table XV.—Initial Terms of 84 PQR.

<i>m.</i>	R (<i>m</i>) — Q (<i>m</i>).	Q(<i>m</i> +1) — P(<i>m</i> +1).	Diff.	Means.	Term Diff.	2nd Diff.
0	—	180·11	—	180·11	F (1) — F (0)	
1	551·06	549·54	+ 1·52	550·30	F (2) — F (1)	370·19
2	920·23	919·12	+ 1·11	919·68	F (3) — F (2)	369·38
3	1,287·44	1,286·90	+ 0·54	1,287·17	F (4) — F (3)	367·49
4	1,655·30	—	—	1,655·30	F (5) — F (4)	368·13
5	2,022·58	—	—	2,022·58	F (6) — F (5)	367·28

Table XVI.—Final Terms of 84 PQR.

m .	$R(m) - Q(m+1)$.	$Q(m) - P(m+1)$.	Diff.	Means.	Term Diff.	2nd Diff.
1	521·85	520·33	+ 1·52	521·09	$f(2) - f(1)$	347·28
2	868·92	867·81	+ 1·11	868·37	$f(3) - f(2)$	347·81
3	1,216·45	1,215·91	+ 0·54	1,216·18	$f(4) - f(3)$	348·94
4	1,565·12	—	—	1,565·12	$f(5) - f(4)$	346·74
5	1,911·86	—	—	1,911·86	$f(6) - f(5)$	

The error in the combination principle looks rather systematic, as though the principle did not apply exactly. There is some slight irregularity about $m = 3$ or $m = 4$ in the second differences, both in the initial and final states, and there is also some systematic variation with m , but both initial and final terms are of the type for which the second differences are very nearly constant.

If we use the formulæ $F(m) = B(m - P)^2$ and $f(m) = b(m - \rho)^2$ the values of P and ρ are very small. In fact, owing to the variations in the second differences of the term numbers just referred to, we cannot be sure that P and ρ are not each of them equal to zero. In these circumstances the most reasonable procedure seems to be to assume that the values of both P and ρ are zero, and to use the resulting relations $3B = F(2) - F(1)$ and $3b = f(2) - f(1)$ to determine B and b . If we do this, we obtain $B = 183·43$ and $b = 173·70$. This value of B compares with a possible value $Ce = 183·24$ for 10 $P(m)$, and with a possible value $Ca = 182·39$ for 152 $R(m)$. Using these values of B and b together with $P = \rho = 0$, we find $F(1) = 183·43$, $F(2) = 733·73$, $f(1) = 173·70$, $f(2) = 694·79$, and the three successive values of ν_0 from $P(2)$, $Q(1)$, and $R(1)$ as 20208·61, 20207·85, and 20208·61 respectively.

The following collection of lines is rather fragmentary.

Table XVII.
Series No. 203 P (*m*).

<i>m</i> .	Properties.							Wave-length in air.		Wave number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)					
2					Z			4928·62	II, 202 P (3)	20284·02 (10)		
3								4936·17		20253·00 (1)	31·02	21·78
			Missing.					—		(20243·76)	9·24	22·26
5	++							4935·25		20256·78 (0)	13·02	23·77
6								4926·30		20293·57 (<i>p</i>)	36·79	

Series No. 104 Q (*m*).

1								4916·28		20334·91 (0)		
2	++		+	+				4908·80	I, III	*20365·89 (2)	30·98	20·38
3	++			+				4896·46	41 Q (0), 58 R (1) II, R (3), I, II, III	20417·25 (2)	51·36	20·25
4								4879·34		20488·86 (<i>r</i>)	71·61	

Series No. 58 R (*m*).

0	++			+				4919·11	II, III	20323·22 (2)		
1	++			+				4896·46	41 Q (0), 104 Q (3) 11 R (3), I, II, III	20417·25 (2)	94·03	19·36
2								4869·42	38 R (2), I, II, III	20530·59 (2)	113·34	18·93
3			—	O				4838·25	II, III	20662·86 (4)	132·27	

* Absent at -252° C. (McL. and S.).

The intensity distribution in these lines is irregular, but perhaps the weakest feature is the heavy duty which is required from the line 20417·25 (2). This line is certainly required as both 104 Q (3) and 58 R (1) in the present combination, and it is also claimed as 41 Q (0) and 11 R (3). Its claim to be 41 Q (0) might conveniently be abandoned without appreciable detriment to that series, but it is difficult to see how 11 R can get along without it. Further investigation of the spectrum might, of course, show that 11 R (*m*) is not a genuine series, but that evidence has not appeared up to the present. 20284·02 (10) is claimed as both 202 P (3) and 203 P (2), but it is a very strong line which may easily cover up both of them. 20530·59 is claimed as both

38 R (2) and 58 R (2) and seems necessary to both of these series. The claim of the fragment exhibited in Table XVII to serious consideration as a band rests mainly on the fact that all the lines of any strength are weakened in the discharges, and on the numerical properties of the term numbers which are given in Tables XVIII and XIX.

Table XVIII.—Initial Terms of 203 P, 104 Q, 58 R.

<i>m.</i>	$R(m) - Q(m).$	$Q(m+1) - P(m+1).$	Diff.	Means.	Term Diff.	2nd Diff.
1	82.34	81.87	+ 0.47	82.11	F (2) — F (1)	82.37
2	164.70	164.25	+ 0.45	164.48	F (3) — F (2)	
3	245.61	—	—	245.61	F (4) — F (3)	81.13

Table XIX.—Final Term Numbers of 203 P, 104 Q, 58 R.

<i>m.</i>	$R(m) - Q(m) + 1$	$Q(m) - P(m + 1)$	Diff.	Means.	Term Diff.	2nd Diff.
0	— 11.69			— 11.69	$f(1) - f(0)$	62.82
1	+ 51.36	50.89	+ 0.47	+ 51.13	$f(2) - f(1)$	61.90
2	+ 113.34	112.89	+ 0.45	+ 113.12	$f(3) - f(2)$	60.88
3	+ 174.00			+ 174.00	$f(4) - f(3)$	58.08
4		$\begin{cases} 232.08 \\ \text{or} \\ 235.86 \end{cases}$		$\begin{cases} + 232.08 \\ \text{or} \\ + 235.86 \end{cases}$	$f(5) - f(4)$ $f(5) - f(4)$	or 61.86

If we apply the equation $F(m) = B(m - P)^2$ to the initial terms they are seen to be of the half-quantum type, the value of P being one-half to within the degree of accuracy to which the data enable the value of B to be assigned with certainty. The first of the two alternatives for $f(5) - f(4)$ in Table XIX is got from the line assigned to 203 P (5) in Table XVII. Owing to the missing line 203 P (4) the correct attribution of this line is uncertain. If the neighbouring line 20253.00 is taken instead, the second set of alternative values at the bottom of Table XIX is obtained. It does not seem possible to decide between these alternatives at present. If we apply the equation $f(m) = b(1 - \rho)^2$ to the final terms, the value of ρ is close to 0.675. This exceeds one-half by much more than any possible error, but it may perhaps be looked upon as an approximation towards the half-quantum type. If we take $B = 42$, $b = 31$, $P = \frac{1}{2}$, $\rho = 0.675$, we find $F(1) = 10.25$, $F(2) = 92.36$,

$f(1) = 3.27$, $f(2) = 54.40$, and the values of ν_0 from P (2), Q (1) and R (1), respectively, are 20328.17, 20327.93 and 20328.16.

The values of B and b deduced in the way just indicated make the moments of inertia of the sources of this band very high; higher, in fact, than those for 1 P, 28 Q, 201 R. It may be that the correct interpretation is not so simple as I have assumed. For example, the jumps might be from a set of states such as $m + \frac{1}{4}$, $m + 1 + \frac{1}{4}$, $m + 2 + \frac{1}{4}$, etc., to a set such as $m - \frac{1}{4}$, $m + 1 - \frac{1}{4}$, $m + 2 - \frac{1}{4}$, or something of the kind. This would have the effect of halving the moment of inertia deduced from the experimental data. Such a possible alternative interpretation should be borne in mind, particularly in view of the fact that the straightforward interpretation leads to term numbers of the half-quantum type. The fact that R (0) occurs in strength may also be important in this connection. Unfortunately, the intensity distribution is so irregular that it affords little help, but it seems a very improbable one for a system with a very high moment of inertia.

This argument might also apply to 1 P, 28 Q, 201 R, for which we calculated $P = 0.54324$ and $\rho = 0.505$. It seems also that the lines 17296.10 (1), ..., ..., ..., ..., ..., and 17299.42 (= 28 Q (1)) may not be entirely excluded as possibilities for 201 R (0).

In a former paper* by the writer and Prof. Tanaka, a possible connection was suggested between the well-marked series 20 Q (m) there described and a series designated as 26 P (m). It seems, however, more likely that the lines associated with 20 Q (m) are those given in Tables XX and XXI.

Table XX.—Series 20 P (m).

m .	Properties.							Wave-length in air.	Wave number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
2								4291.17 (T)	23297.15 (g)		
3				+				4361.90	†22919.37 (0)	377.78	14.36
4								4432.18	22555.95 (0)	363.42	14.05
5				+	O			4501.91 I, II, III	22206.58 (3)	349.37	14.24
6								4570.89 (T)	21871.45 (rd)	335.13	15.96
7								4638.58 60 R (5)	21552.28 (0)	319.17	

* 'Roy. Soc. Proc.,' A, vol. 107, p. 614 (1925).

† Measured by M. and B. on one plate only.

Table XXI.—Series 20 R (m).

m .	Properties.							Wave-length in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
1		+						4066·90	24581·86 (4)		
2								4000·28	24991·19 (0)	409·33	14·06
3								3933·64 (T)	25414·58 (0)	423·39	8·03
4								3867·98 (T)	25846·00 (p)	431·42	9·80
5		++						3803·05	26287·22 (2)	441·22	

The only line of any strength in the P series is weakened in each type of discharge. The very faint diffuse line assigned to 20 P (6) was originally measured by Prof. Tanaka as 21871·45. It has since been remeasured by Mr. Williams, who gives it the wave-number 21871·75. The mean of these values, 21871·60, has been used in the computations leading to Tables XXII and XXIII below. The line 21552·28 (0) is also claimed by 60 R (5). It seems rather strong as 20 P (7), but the distribution of intensity in 20 P (m) is irregular, and there seems some indication of the alternations of strength with odd and even values of m which is so characteristic of 20 Q (m). None of the lines in 20 R (m) have been recorded as weakened lines, but it is intended to re-examine this part of the spectrum. The correct assignation of 26287·22 to this series is very improbable. A line which would do just as well is a weak line 26293·72 (p), wave-length in air 3802·11; but neither of them satisfies the combination principle. The second differences look very variable, especially those of 20 R (m), but it should be remembered that the second differences of 20 Q (m) varied in a quite regular manner between the limits 10·59 and 13·69, so that it is to be expected that any associated series will show similar variations.

If these lines are a band and satisfy the combination principle, the initial and final term numbers, etc., are given in Tables XXII and XXIII.

Table XXII.—Initial Term Numbers of 20 PQR.

m .	$R(m) - Q(m)$.	$Q(m+1) - P(m+1)$.	Diff.	Term Diff.	Means. 2nd Diff.	Values from 2nd Diff. PQ only.
1	648·17	647·49	+ 0·68	F (2)—F (1)	647·83	647·49
2	1046·55	1047·31	— 0·76	F (3)—F (2)	1046·93	1047·31
3	1447·90	1445·93	+ 1·97	F (4)—F (3)	1446·91	1445·93
4	1844·12	1844·19	— 0·07	F (5)—F (4)	1844·16	1844·19
5	2236·45 or 2242·95	2239·95	— 3·50 or + 3·00	F (6)—F (5)	2239·95	2239·95
6		2630·64		F (7)—F (6)	2630·64	2630·64

* Value from R (5) — Q (5) not used.

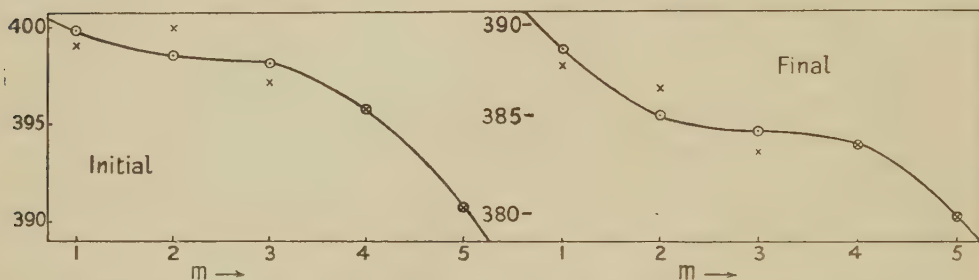
Table XXIII.—Final Terms of 20 PQR.

m .	$R(m) - Q(m+1)$.	$Q(m) - P(m+1)$.	Diff.	Term Diff.	Means. 2nd Diff.	Values from 2nd Diff. PQ only.
1	637·22	636·54	+ 0·68	$f(2) - f(1)$	636·88	636·54
2	1024·51	1025·27	— 0·76	$f(3) - f(2)$	1024·89	1025·27
3	1412·70	1410·73	+ 1·97	$f(4) - f(3)$	1411·71	1410·73
4	1795·23	1795·30	— 0·07	$f(5) - f(4)$	1795·27	1795·30
5	2175·67 or 2182·17	2179·17	— 3·50 or + 3·00	$f(6) - f(5)$	*2179·17	2179·17
6		2559·27		$f(7) - f(6)$	2559·27	2559·27

* Values from R (5) — Q (6) not used.

As there appear to be some irregularities in this R series the values from the P and Q combinations alone, as well as from the means of the PQ and RQ combinations, are given in this table. In any event the line 20 R (5) which is either non-existent or displaced has not been used in the computations. The second differences from the PQ combinations seem more regular than those got from the means. They are peculiar in that the third difference at first diminishes and then increases again as m increases. This behaviour is shown in the diagram. The alternatives given under $m = 5$ in the RQ combinations depend on whether R (5) is taken as the line 26287·22 (2) given in Table XXI or the alternative line 26293·72 (p). As will be seen neither line satisfies the combination principle and most probably both ought to be excluded.

With the second differences following a function like the graph shown, it is difficult to know what precise value to assign to B and b . If as a first approxi-



20 PQR.—Second diffs. of Term Numbers. $\times$ from means. $\odot$ from P and Q only.

mation we assume the equations $F(m) = B(m - P)^2$ and $f(m) = b(m - \rho)^2$ to apply, and put $B = 200$, $B(3 - 2P) = F(2) - F(1) = 647.49$, we find $P = -0.1187$. Putting $b = 194$, $b(3 - 2\rho) = 636.88$ we obtain $\rho = -0.1414$. Thus both P and ρ come out negative for this combination. With these values of B , b , P and ρ the term numbers for small values of m are $F(0) = 2.82$, $F(1) = 250.30$, $F(2) = 897.78$ and $f(0) = 3.88$, $f(1) = 252.74$, $f(2) = 889.61$. The values of ν_0 obtained from P (2) Q (1) and R (1), respectively, are 23936.86, 23936.13 and 23936.82. There are about 6 cm^{-1} higher than the value previously got* from 20 Q (m) assuming the 20 Q (m) 26 P (m) combination to be valid.

The calculated positions of 20 P (1), 20 Q (0) and R (0) using ν_0 , $F(0)$, $F(1)$, $f(0)$ and $f(1)$ are at 23686.6, 23935.4 and 24182.9 respectively. The nearest lines to these are 23692.92 (0), wave-length in air 4219.49 (T), 23939.42 (τ), wave-length in air 4176.04 (T), and 24182.92 (0) which has already been assigned to 20 Q (7). Thus P (1) and Q (0) certainly, and R (0) probably, do not exist. These lines correspond to the rotational quantum transitions $m = 0$ to $m = 1$, $m = 0$ to $m = 0$ and $m = 1$ to $m = 0$, and their non-existence is in agreement with the non-existence of the non-rotating state which is normally required by the correspondence principle. In this band the Q series is much the strongest and the distribution of intensity amongst its lines (the maximum is at $m = 1$) is in satisfactory agreement with the low values of the initial and final moments of inertia corresponding to values of B and b in the neighbourhood of 200.

The following lines appear to form a Q series :—

* Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 107, p. 615 (1925).

Table XXIV.—Series 85 Q (m).

m .	Properties.							Wave-length in Air.		Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)					
0				++	0			4379.38	I, II m ,	III 22827.87 (2)		
1				++	0		S	4390.89	I, II26P (3),	III 22768.05 (2)	59.82	60.49
2				++	0		S	4414.22	I, II,	III 22647.74 (2)	120.31	61.42
3	+							4449.92	II,	III 22466.01 (1)	181.73	60.97
4				+	0			4498.52		22223.31 (2)	242.70	57.86
5?		++						4560.20		21922.75 (0)	300.56	

The properties of the lines seem fairly homogeneous, and the first four are all weakened in the second and third type discharges and the first three in the first type also. The second differences show considerable variation, but the variation is regular. 22768.05 is claimed also by 26 P (3), but it may be too strong as 85 Q (2) if the indications of alternation in intensity are substantiated. The lines can be represented as a half-quantum series of the type given by $Q(m) = \nu_0 + Cd/4 + Cd m + Cd m^2$ with the enumeration assigned in the table. The approximate values of ν_0 and Cd are $\nu_0 = 22835.5$ and Cd (not constant) about -30 . The assigned enumeration might have to be amended if the associated P and R series are found.

For convenience of reference the essential data of the series dealt with in this paper are collected together in Table XXV. It should be borne in mind that many of the numbers are subject to some degree of uncertainty, depending on the fact that in certain instances the data are inadequate to settle the interpretations absolutely. In making use of them, therefore, it is desirable that the discussion in the text should be taken into consideration.

Table XXV.

Series No.	ν_0 .	B	b	P	ρ	Ca	Ce	Ca-Ce
159 R 159 Q	15961·9	168·46	210·10	$\frac{3}{4}$	1			
159 R 159 Q'	15804·64	230	271	0·564	0·564			
152 R	16535·4					175·30	189·48	
	or					or	or	
	16349·5					182·39	196·57	
185 PQR	20486·9	164·28	157·26	0	0			
111 P 61 Q	22536·4	50	68	0·44	0·37			- 18
204 R								•
112 Q	22545 app.			1 app.	1 app.			+ 18·60
84 PQR	20208	183·43	173·70	0	0			
202 P 104 Q	20328	42	31	$\frac{1}{2}$	0·675			
58 R								
20 PQR	23936·5	200	194	-0·1187	-0·1414			
85 Q	22835·5			$\frac{1}{2}$	$\frac{1}{2}$			- 30

I propose to postpone the further consideration of these lines until the description of another lot, which have been arranged provisionally in series, has been completed.

I am indebted to Prof. Tanaka in connection with the series 111 P (*m*) 61 Q (*m*) 112 Q (*m*), 58 R (*m*) and 104 Q (*m*) first published in this paper. These were obtained, mainly by Prof. Tanaka, when we were working together, but there did not seem to be any sufficient justification for publishing them at the time. I am also very grateful to Mr. W. E. Williams, who has kindly re-examined or re-measured a considerable number of the lines whose status seemed doubtful.

The Kinetic Theory of Surface Films. Part I.—The Surfaces of Solutions.

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§1. *The Basis of the Traube-Langmuir Theory.*

A study of the catalytic properties of solid surfaces has led to a belief that the distance at which molecules cease to attract one another appreciably is of the same order of magnitude as the diameter of an atom, a distance much smaller than that imagined by Laplace. On the Laplacian view the transition between liquid and vapour at a phase-boundary is gradual, but on the newer theory the non-homogeneous layer separating the homogeneous phases is little, if at all, greater than the diameter of a molecule. The work of Langmuir (1) on the influence of small quantities of certain insoluble organic substances upon the surface tension of water* supports the latter view. The substances which are found to act in this way are hydrocarbons in which has been substituted an "active" group, such as COOH or OH. These groups tend to make the substance soluble in water, but the substitution of only one of them in a hydrocarbon containing more than twelve carbon atoms in the molecule is insufficient to cause any appreciable solution. Langmuir suggests that molecules of, say, palmitic acid placed on water orientate themselves, so that the COOH group is in the liquid phase while the hydrocarbon chain is in the vapour phase, a condition which is only realizable if the phase boundary is relatively sharp. His well-known trough experiments (2) amply support this idea, and confirm the necessary corollary: that a water surface of a given area can only accommodate a limited number of orientated molecules. N. K. Adam (3), in repeating and extending Langmuir's experiments with more refined apparatus, has shown that the least area occupied by these molecules is in excellent agreement with that to be expected from the recent X-ray determinations of Sir William Bragg.

In the paper in which his work on insoluble films is described Langmuir also deals with the lowering of the surface tension of water by soluble substances (4), such as the fatty acids and alcohols of small molecular weight. He suggests

* The pioneer work in this field was done by Miss Pockels, Lord Rayleigh, and Devaux; but to Langmuir is due the credit for fully realising the light which the phenomenon throws on the structure of liquid surfaces.

that the excess concentration of solute, which an application of Gibbs' adsorption equation shows to exist in the neighbourhood of the phase boundary, is present as a single layer of molecules, orientated partially or completely like those of insoluble substances. In support of this he quotes a paper by Milner (5), where it is shown that soluble substances which depress the surface tension of water appear to give a surface excess reaching a constant limiting value for large depressions. This conclusion is drawn from the fact that the relation

$$\sigma_0 - \sigma = \alpha + \beta \log_{10} N \quad (i)$$

is found to represent the behaviour of solutions of acetic acid for large values of $\sigma_0 - \sigma$. In this equation σ is the surface tension of the solution, while σ_0 is that of pure water; N is the molar fraction of the solute, and α and β are constants.

Equation (i) when differentiated gives

$$\frac{d\sigma}{d \log_{10} N} = -\beta. \quad (ii)$$

For ideal solutions Gibbs' adsorption equation takes the form

$$\Gamma = -\frac{N}{RT} \cdot \frac{d\sigma}{dN} = -\frac{d\sigma}{2.303 RT d \log_{10} N} \quad (iii)$$

so that if these solutions be regarded as ideal

$$\Gamma = \frac{\beta}{2.303 RT} \quad (iv)$$

over the range for which Milner's equation holds.

This value of Γ corresponds, in the case of acetic acid, to an area per molecule of 43 Å.U. Langmuir appears satisfied with the agreement between this value and 20–25 Å.U. found for films of the insoluble acids,* though the discrepancy cannot be attributed to experimental error.

* Langmuir also employs the empirical relation

$$\frac{\sigma_0 - \sigma}{\sigma_0} = b \log_{10} \left(\frac{N}{N_0} + 1 \right)$$

where b and N_0 are constants, put forward by Szyszkowski ('Zeits. Phys. Chem.', vol. 64, p. 385 (1908)), to determine the limiting value of Γ . If N is large compared with N_0 , this equation approximates to that of Milner and

$$\Gamma_{\text{limit}} = \frac{b}{2.303 \sigma_0 RT}.$$

This gives a limiting area 31 Å.U. per molecule for butyric acid, a substance for which the data are in good agreement with von Szyszkowski's equation. If N is small compared with N_0 the right-hand side of von Szyszkowski's equation is approximately proportional to N . This agrees with the observation of Traube (*vide infra*). This equation may be regarded as a link between those of Traube and Milner. In practice, however, it does not represent the experimental data of most substances well enough to be of much value.

From this evidence he concludes (6) that a water surface whose tension is considerably reduced is covered by a closely-packed orientated film of molecules, whether the active substance is soluble or insoluble ; but he points out one respect in which soluble and insoluble films differ from one another. The surface of solutions which by equation (iii) have a value of Γ of 2×10^{-10} gram. mols. per sq. cm., give values of $\sigma_0 - \sigma$ which vary from 5 to 10 dynes per cm. at 20°C . The same number of molecules of an insoluble substance, put on 1 sq. cm. of water surface, would not cause the surface tension to be decreased by as much as one-tenth of a dyne per cm. To explain this Langmuir resuscitates a theory of Traube (7). The latter found that the quantity F defined by

$$F = \sigma_0 - \sigma \quad (\text{v})$$

is approximately proportional to the bulk concentration for small values of F , or

$$F = \kappa N. \quad (\text{vi})$$

If the solution be regarded as ideal this combined with (iii) gives

$$F \cdot 1/\Gamma = RT,$$

or, writing $A = 1/\Gamma$ for the area occupied by a gram. mol. as surface excess,

$$FA = RT. \quad (\text{vii})$$

The resemblance between this equation and the equation $pv = RT$ for a perfect gas led Traube to suggest that the lowering of the surface tension of a solvent by a solute is due to the thermal agitation of the solute molecules adsorbed at the surface. The observed surface tension is on this view the resultant of two forces : one the unaltered tension of the solvent surface and the other an outward two-dimensional "gas" pressure exerted by the solute molecules in excess at the interface. According to Langmuir the failure of insoluble films to show this "gas" pressure is due to the considerable lateral attraction between hydrocarbon chains sufficiently long to cause insolubility, in consequence of which these films resemble liquids more than gases. The possibility of the existence of surface films showing properties resembling the three states of matter had previously been suggested by Devaux (8). To this Langmuir adds that "surface liquids" may exert a "vapour pressure," though this must be less an 0.1 dynes per cm. for all insoluble films so far investigated. He also considers that critical phenomena are to be expected.

§ 2. *The Unsatisfactory Nature of the Evidence brought forward in support of the Traube-Langmuir Theory.*

It must, however, be admitted that, apart from the general reasonableness of Langmuir's views, the evidence submitted in attempting to explain the lowering of the surface tension of solutions on kinetic grounds is far from satisfactory, and has, indeed, been rejected by some people. The proportionality between F and N is the only argument cited in favour of the hypothesis. By itself this proportionality is insufficient to establish any theory, especially seeing that it is not even approximately obeyed for large values of F . Again, the limiting molecular areas determined by Milner's or von Szyszkowski's equations, although of the same order of magnitude, are considerably larger than those to be expected, assuming the Gibbs' layer to consist of a single layer of orientated molecules of a size computed from a study of insoluble films or from X-ray measurements.

A theory, to be convincing, must explain not only the proportionality between F and N for small values of F , but also the lack of proportionality for large values. If, therefore, the kinetic explanation is to be satisfactorily established, it must not only be capable of explaining why FA/RT approximates to unity for small values of F , but must also give a satisfactory account of its departure from unity as F increases. The possibility that this departure is due to the same causes that render both the Boyle-Charles law inapplicable to highly compressed gases, and the simple Van't Hoff law inapplicable to strong solutions, has led the writers to undertake a review of the existing data in this light.

§ 3. *The Limitations in the Methods available for the Evaluation of F and A .*

Langmuir's trough method gives directly the values of F and A for capillary active substances which are insoluble in both the phases adjoining the interface. For substances which are soluble in either one or both the adjoining phases these quantities have to be evaluated indirectly from surface-tension data. It is therefore necessary, before basing any conclusions upon the values of FA/RT calculated in this way, to consider how far the indirect method of determination is to be relied upon.

Gibbs' (9) adsorption equation, which is based solely on thermodynamic reasoning, may be written thus:—

$$d\sigma = - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \text{etc.} \quad (\text{viii})$$

for a system at constant temperature. This relation connects the change in surface tension σ of an interface with the corresponding changes in the chemical

potentials μ_1, μ_2 , etc., of the independently variable components of the system. Γ_1, Γ_2 , etc., are the excess surface concentrations of these components, reckoned with respect to an imaginary geometrical surface which is parallel to, but not necessarily coincident with, the physical surface of discontinuity. Gibbs called this imaginary surface the dividing surface.

The sum of the terms on the right-hand side of equation (viii) does not depend on the position chosen for the dividing surface, but this is not true of the individual terms, any one of which can be made zero by a suitable choice. When this is done for the surface of a binary mixture, and the term referring to one component (which we will call the solvent and designate by the suffix 1) disappears, we are left with the equation

$$d\sigma = -\Gamma_2 d\mu_2$$

or

$$\Gamma_2 = -d\sigma/d\mu_2. \quad (\text{ix})$$

This equation enables us to determine the surface excess of the solute with respect to a dividing surface which gives no surface excess of solvent. Henceforth this quantity will be called simply Γ .

It is frequently assumed that solutions in contact with an interface are ideal, or that for each constituent

$$d\mu = 2.303 RT d \log_{10} N$$

where N is the molar fraction. If such were the case equation (ix) would become

$$\Gamma = -\frac{d\sigma}{2.303 RT d \log_{10} N_2}. \quad (\text{x})$$

When dealing with strong solutions of non-electrolytes, or even weak solutions of electrolytes, such an assumption is not justified, but in these cases the form of equation (x) may be retained by replacing N by the activity a . The Gibbs' equation then becomes

$$\Gamma = -\frac{d\sigma}{2.303 RT d \log_{10} a_2}$$

$d \log a_2$ being defined by the equation

$$d \log_{10} a_2 = d\mu_2/2.303 RT.$$

Thus the true values of Γ may be determined for a solution over the range of concentrations for which the surface tensions and activities are known.

There are very few binary mixtures for which there are sufficient data to calculate the values of Γ at the liquid-vapour interface over a wide range of concentration, but this has been found possible in the case of mixtures of ethyl

alcohol and water by combining the surface-tension data of Bircumshaw (10) at 25° C. with the corresponding values of the partial vapour pressures of ethyl alcohol intrapolated from the data of Kononov (11) and Wrewski (12). Regarding water as the solvent, we may determine Γ for the alcohol by the equation

$$\Gamma = - \frac{d\sigma}{2 \cdot 303 RT d \log_{10} p}$$

which is nearly exact at this temperature, by plotting σ against $\log_{10} p$, and finding the slopes of tangents to the curve.

The resulting values are plotted against the molar fraction of alcohol in fig. 1, and a dotted curve, which gives the values obtained by assuming perfect solution and using equation (x), is added for comparison. The curves are probably accurate to a few per cent., the middle portions being most uncertain. The numerical data are given in Table I.

The true Γ -N curve is evidently divisible into two portions. On increasing N_2 , Γ rises rapidly at first, then more slowly, and appears to be approaching a

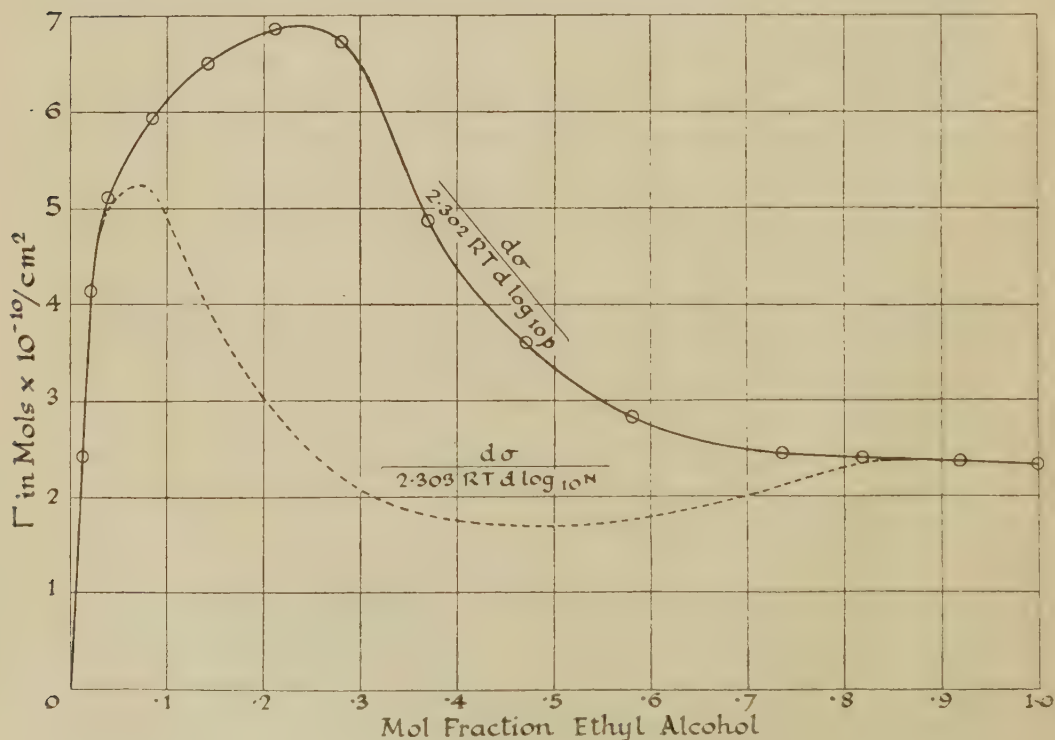


FIG. 1.

Table I.

Weight, per cent.	Mol. Fraction N.	Partial Vapour Pressure p .	Log p/p_0 .	Surface Tension.	$-\frac{d\sigma}{2.303 RT d \log_{10} p}$.	$-\frac{d\sigma}{2.303 RT \log_{10} N}$.
		Millimetres.		dynes/cm.		
0.00	0.0000	—	—	72.20	—	—
2.22	0.0108	1.9	2.508	60.79	3.28	—
5.21	0.0210	3.8	2.798	54.87	4.13	—
11.10	0.0466	8.3	1.136	46.03	5.10	—
20.50	0.0917	16.8	1.415	37.53	6.00	5.05
30.47	0.1463	21.8	1.554	32.25	6.53	3.76
40.00	0.2078	25.8	1.628	29.63	6.80	2.88
50.22	0.2826	28.6	1.674	27.89	6.75	2.12
59.58	0.3657	31.3	1.712	26.71	4.92	1.93
68.92	0.4645	34.3	1.753	25.71	3.26	1.70
77.98	0.5808	39.0	1.807	24.73	3.01	1.83
87.92	0.7387	36.1	1.880	23.64	2.45	2.01
92.10	0.8202	50.4	1.919	23.18	2.41	2.38
97.00	0.9274	56.5	1.969	22.49	2.40	2.40
100.00	1.0000	60.7	0.000	22.03	2.40	2.40

maximum value. When N_2 has reached 0.3, however, a new change sets in, for the remaining portion of the curve shows a value of Γ which falls to a steady value for nearly pure alcohol. If Langmuir's hypothesis be applied to the maximum value of Γ an area per molecule of 24 Å.U. is obtained. This value is considerably closer to the value 21.6 Å.U. to be expected for a close-packed vertically orientated film than 33 Å.U. obtained from Milner's equation. This last value corresponds to the maximum of the dotted curve, and this shows the errors involved in assuming the laws of ideal solution.*

The second portion of the curve is not readily interpreted, for calculating on this basis the area occupied by each of the excess alcohol molecules a value 69 Å.U. is obtained. It is possible, without rejecting the hypothesis of a uni-molecular surface film, to attribute the increase in molecular area to a decrease in the degree of orientation of the alcohol molecules in the outermost layer, when the less polar alcohol replaces the more polar water in the underlying liquid. Alternatively, we may consider the formation in strong alcohol solutions of a layer relatively rich in water below the surface layer of adsorbed alcohol, the water being held by the hydroxyl groups of the upper layer of orientated alcohol molecules. Since the dividing surface is so chosen that the total quantities of

* A lack of appreciation of the fact that the activity of solutions of sodium oleate hardly increases at all as their strength is increased (except for exceeding small concentrations) has led to erroneous conclusions being drawn for the constancy of the surface tension of all but the weakest solutions.

alcohol and water beneath it bear the same ratio to one another as they do in a homogeneous portion of the liquid, in order to compensate the excess of water this surface will also include some of the alcohol in the outermost layer. Γ will in this case be the amount of alcohol outstanding and not the total quantity in the outermost layer. We have no means of deciding between these two explanations; indeed, neither of them may be altogether correct, but the fact that the change in surface tension from $N = 0.3$ to $N = 1$ is only 6 dynes per cm., as against 44 dynes per cm. for the rest, lends support to a theory which does not involve so drastic an alteration in the arrangement of the surface molecules as is required by that first proposed.

Whatever the uncertainties may be in strong solutions, the finite value which Γ approaches in weak solutions indicates that the concentration of solute in the Gibbs' layer cannot exceed a certain finite value, whence it follows that this layer cannot be of indefinite thickness. Although the disturbing influences which cause a fall in Γ for large values of N_2 prevent the limiting value from being attained, the course of the *true* Γ - N curve for weak solutions is entirely consistent with the view that here the Gibbs' layer is but one molecule thick, and that Γ is approaching the value for a single layer of close-packed orientated alcohol molecules.

It is sometimes objected that the rate of evaporation and condensation at an air-liquid interface may be so rapid as to prevent the orientation of the molecules in the Gibbs' layer. In the foregoing example this would be more marked for solutions rich in alcohol, and the apparent increase in molecular area might be attributed to this cause. Against this view it may be pointed out that the Γ - N curve for pyridine adsorbed at a mercury-water interface, shown in fig. 2, also gives a surface excess which decreases in strong solutions. In this case rapid exchange with a vapour phase is absent, the only exchange being that of the pyridine in the Gibbs' layer and in the solution. The surface-tension data used for obtaining fig. 2 are those of Gouy (13) for the surface tensions at the maxima of the electro-capillary curves.* The vapour-pressure measurements of Zadwiski (14) at 96° C. have been used. The extrapolation to 18° C. involves uncertainties, but the general shape of the Γ - N curve is quite clear.

The determination of F is also accompanied by some uncertainties, since its evaluation involves a computation of the effect which the presence of the Gibbs'

* At the maximum of an electro-capillary curve the mercury surface is uncharged. It is only in this condition that the interface exhibits true adsorption undisturbed by electrical effects. A lack of attention to this point renders useless most of the observations on this interface.

layer has on the surface tension. It is strictly defined as the difference between the surface tension of the solution with the Gibbs' layer established and that

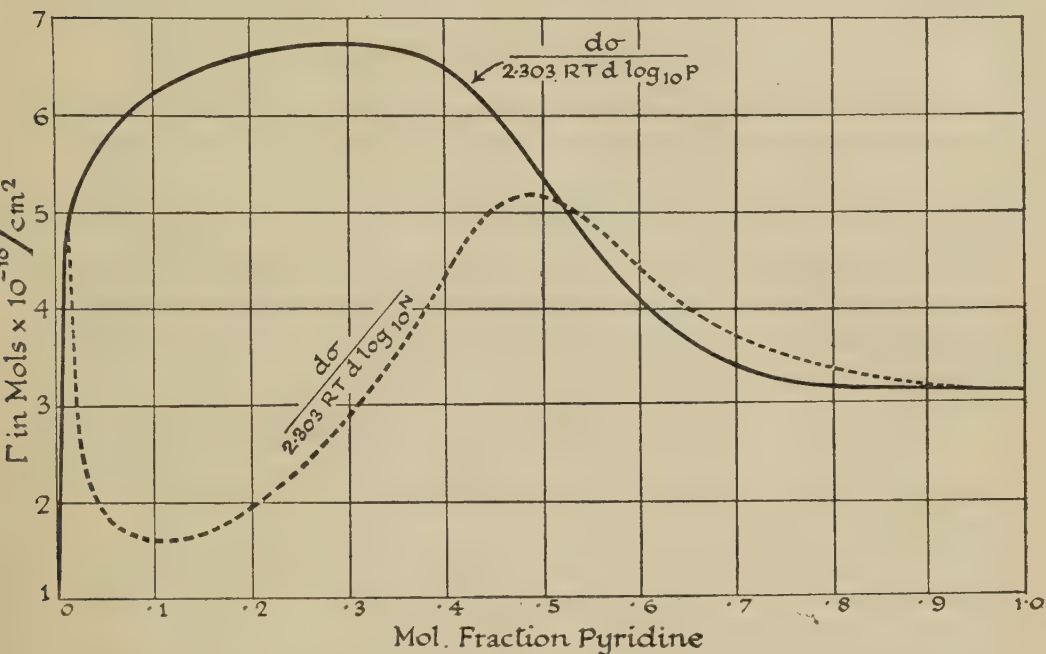


FIG. 2.

of the solution with no surface excess. In the case of very dilute solutions σ_0 can be regarded as the surface tension of the pure solvent, but this cannot be justified for strong solutions. It is possible that an elaboration of the dynamical methods for the measurement of the surface tension of mixtures might lead to an accurate means of determining F for strong solutions.

§ 4. The evaluation of FA/RT for Weak Solutions of Capillary Active Substances.

Having discussed the limitations in the indirect determination of F and A for strong solutions, we see that these do not apply to dilute solutions of substance which are sufficiently capillary active to be studied under these conditions. In such cases σ_0 is the surface tension of the pure solvent, so that

$$d\sigma = -dF,$$

Gibbs' equation, which may be written

$$A = \frac{1}{\Gamma} = -\frac{d\mu_2}{d\sigma}$$

thus becoming

$$A = d\mu_2/dF$$

whence

$$\frac{FA}{RT} = \frac{F}{RT} \cdot \frac{d\mu_2}{dF} = \frac{d\mu_2}{2 \cdot 303 RT} \cdot \frac{1}{d \log_{10} F}.$$

For $d\mu_2/2 \cdot 303 RT$ may be substituted $\log_{10} \gamma C$, where C is the concentration of the active substance in mols. per litre and γ is the activity coefficient, whence

$$\frac{FA}{RT} = \frac{d \log_{10} \gamma C}{d \log_{10} F}. \quad (\text{xi})$$

von Szyszkowski (15) has made careful determinations of the surface tensions of solutions of butyric, valeric and caproic acids at a number of concentrations. For these solutions, γ is unity at all but the smallest concentrations where a small correction has to be introduced owing to electrolytic dissociation.*

Table II gives the values of $\frac{\Delta \log \gamma C}{\Delta \log F}$ between successive concentrations set against mean values of F , and the resulting curves are shown in figs. 3 and 4.

* For very weak electrolytes the degree of dissociation found by the freezing-point methods agrees with that found from conductivity within the limits of experimental error, and Ostwald's dilution law is obeyed.

When the concentration C of a solution changes, the change in potential of the water is given by

$$d\mu_1 = - \frac{RT}{55 \cdot 51} d[C(1+a)] \quad (55 \cdot 51 \text{ being the number of mols. in 1,000 grs. of water}).$$

The corresponding change in the potential of the solute in dilute solution is

$$d\mu_2 = - \frac{N_1}{N_2} d\mu_1 = - \frac{55 \cdot 51}{C} d\mu_1 = RT \frac{d[C(1+a)]}{C} = RT \left[\frac{dC}{C} + a \frac{dC}{C} + da \right].$$

Integrating this we obtain

$$\frac{\Delta \mu_2}{2 \cdot 303 RT} = \Delta \log_{10} \gamma C = \Delta \log_{10} C + \int_C^{C+\Delta C} a d \log_{10} C + \frac{\Delta a}{2 \cdot 303}.$$

The definite integral may be approximately evaluated if a does not exceed 0.1 by using the approximate Ostwald equation $a^2C = K$, or $C = K/a^2$, whence

$$d \log_{10} C \doteq - 2d \log_{10} a = - \frac{2da}{2 \cdot 303}.$$

The last two terms, which give the value of $\Delta \log_{10} \gamma$, thus reduce to

$$- \frac{2\Delta a}{2 \cdot 303a} + \frac{\Delta a}{2 \cdot 303a} = - \frac{\Delta a}{2 \cdot 303a};$$

whence

$$\Delta \log_{10} \gamma \doteq - 0 \cdot 4343 \Delta \sqrt{K/C}.$$

K for the higher fatty acids, determined by conductivity measurements, is approximately $1 \cdot 5 \times 10^{-5}$.

Table II.

Normal Butyric Acid.		Isobutyric Acid.		Normal Valeric Acid.		Isovaleric Acid.		Normal Caproic Acid.		Isocaproic Acid.	
F.	FA/RT.	F.	FA/RT.	F.	FA/RT.	F.	FA/RT.	F.	FA/RT.	F.	FA/RT.
5.4	1.02	6.0	1.15	3.5	1.00	3.5	1.00	4.4	0.95	2.8	0.89
7.7	1.24	7.5	1.28	5.3	1.02	6.4	1.08	9.2	1.03	4.6	0.89
10.6	1.34	10.1	1.41	7.8	1.12	9.5	1.29	13.2	1.23	7.2	0.99
14.0	1.57	12.3	1.52	11.0	1.26	11.7	1.38	16.6	1.38	10.8	1.14
17.9	1.74	15.5	1.74	14.9	1.50	13.5	1.52	21.4	1.74	14.9	1.42
22.1	2.07	18.5	1.87	19.2	1.80	15.4	1.64	25.3	2.00	19.5	1.64
26.6	2.31	21.7	1.97	23.6	2.05	18.1	1.83	28.2	2.13	24.5	2.04
31.4	2.62	23.4	2.18	28.5	2.39	20.4	1.89	30.6	2.24	29.4	2.48
36.2	3.09	25.7	2.36	33.6	2.63	22.4	2.13	34.3	2.73	34.4	2.68
		28.4	2.59			28.1	2.50	37.3	2.89	39.5	3.10
		30.4	2.62			30.2	2.57				
		33.6	2.80								
		36.1	3.08								
		38.2	3.55								

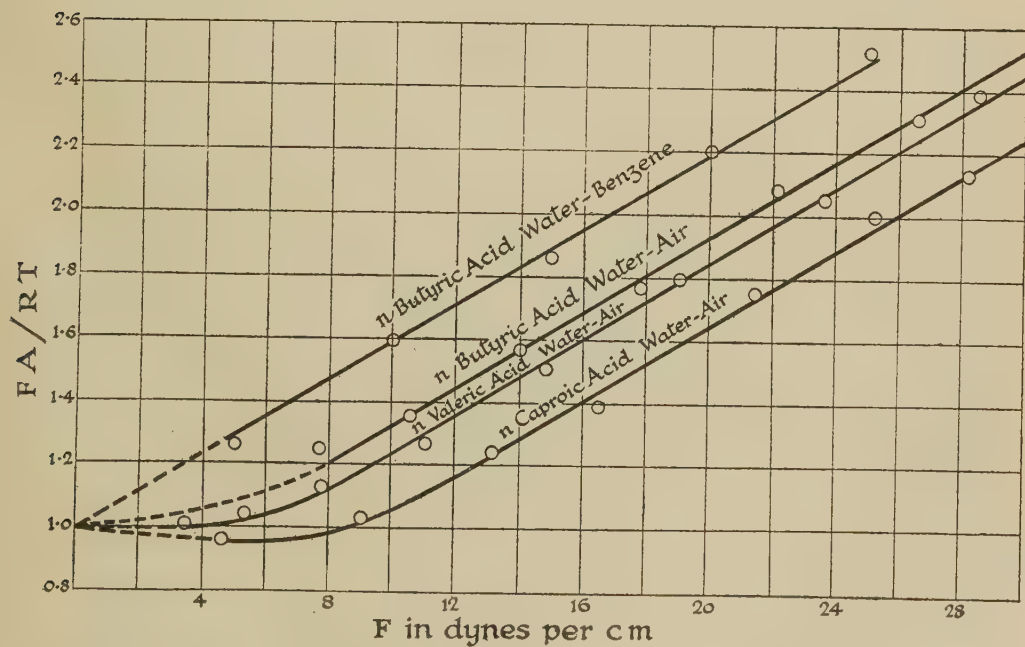


FIG. 3.

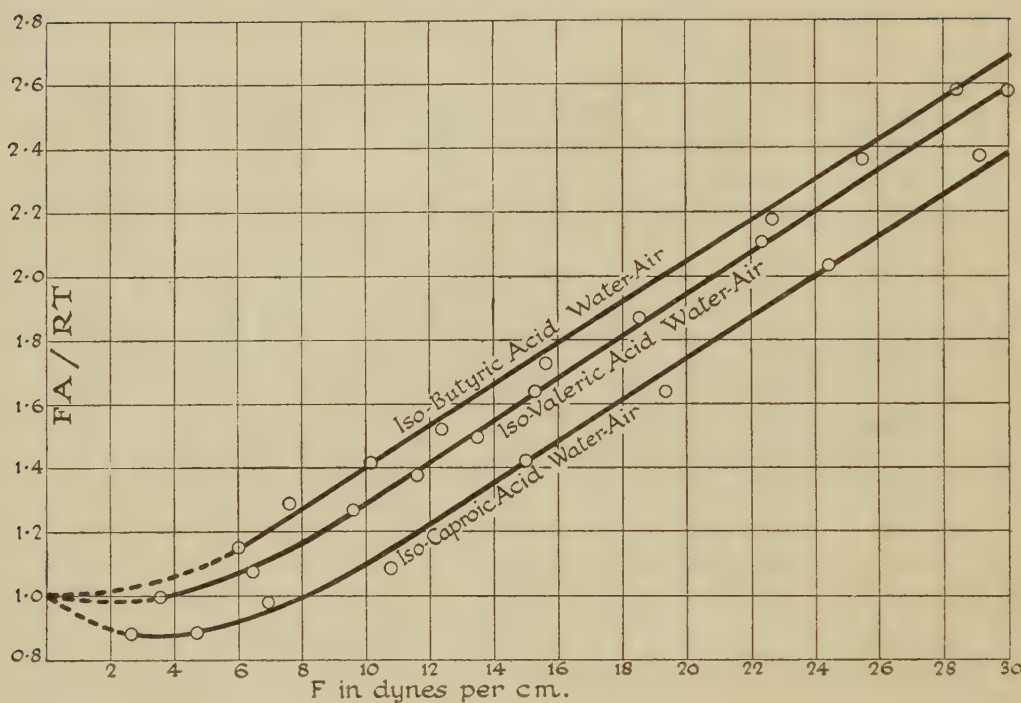


FIG. 4.

§ 5. An Equation of State for Surface Films.

If the adsorbed molecules are confined to a plane it is clear that they cannot be expected to behave like *perfect* gases, whose molecules are supposed to be infinitely small compared with the free space separating them. For at all but the smallest values of F , A is not much larger than the least area that a mol. can occupy under high compression. A considerable variation in FA/RT is thus quite consistent with a kinetic theory. Further than this the general resemblance between the curves of figs. 3 and 4 and the $pv/RT - p$ curves for highly-compressed gases such as hydrogen and nitrogen is apparent. For high pressures the curves as determined by Amagat for gases are straight, and can thus be represented by an equation (16)

$$\frac{pv}{RT} = \frac{b}{RT} \cdot p + x. \quad (\text{xii})$$

In this equation b is a constant for any one gas and is the least volume the gas can occupy. On the other hand x varies both with the nature of the gas and with the temperature, always approaching unity when this is high and becoming smaller as the critical temperature is approached.

Since the $FA/RT - F$ curves are also straight when F exceeds 10 dynes per centimetre a corresponding equation

$$\frac{FA}{RT} = \frac{B}{RT} \cdot F + x \quad (\text{xiii})$$

will reproduce the behaviour of surface films for all but the smallest values of F . Here B represents the least area that a mol. can occupy and $1/x$ is a measure of the molecular cohesion.

Table III.

Substance.	Interface.	B.		x .	Observer.
		Sq. cm. per mol. $\times 10^9$.	Sq. cm. per mol. $\times 10^{-16}$.		
<i>n</i> -Butyric acid	Water-air	1.47	24.3	0.73	Von Szyszkowski.
<i>n</i> -Valeric acid	"			0.63	
<i>n</i> -Caproic acid	"			0.43	
Iso-Butyric acid	"			0.78	
Iso-Valeric acid	"			0.68	
Iso-Caproic acid	"	1.52	25.1	0.48	"
Iso-Amyl alcohol	"	1.36	22.4	0.59	"
<i>n</i> -Butyric acid	Water-benzene	1.45-1.50	24-25	1.00-0.95	Harkins and King
Tertiary butyl alcohol	Water mercury	1.45	24.0	0.52	
Tertiary amyl alcohol...	"	1.69	28.0	0.46	
Cane sugar	"	4.41	72.7	1.00	
Pyridine	"	(1.58)	(26.0)	(1.00)*	"

* These values are only approximate owing to the absence of activity data.

The values of B and x for the substances studied by von Szyszkowski are given in Table III, to which has been added the value of these constants for butyric acid at a water-benzene interface, found from the measurements of Harkins and King (17). In this case a graphical method was employed, as the determinations (which are difficult to make) are not so accurate as those of von Szyszkowski. F was plotted against $\log_{10} C$, a smooth curve was drawn through the points and FA/RT was calculated from the slope S of the curve by the relation

$$\frac{FA}{RT} = \frac{F}{RT} \cdot \frac{2.303 RT d \log_{10} C}{dF} = 2.303 \frac{F}{S}.$$

The results are given in Table IV and the derived curve $FA/RT = 2.303 F/S$ is shown in fig. 3 above.

Table IV.—*n*-Butyric Acid.—Water-Benzene 25° C.

(1)	(2)	(3)
F.	S.	FA/RT.
5	9.2	1.25
10	14.6	1.58
15	18.6	1.86
20	21.4	2.15
25	22.8	2.52

All three normal acids show practically the same value of *B* at an air-water interface, a value which gives a mean area per molecule of 24.3 ± 0.3 Å.U. Substantially the same is given by normal butyric acid at a water-benzene interface. It is practically identical with the value given by Adam for a condensed film* of palmitic acid under zero compression. The best mean value of *B* for the iso-acids which have branched chains is a little larger than that for the normal acids.

The values of *x* show that these acids resemble gases whose critical temperatures increase as the carbon chain lengthens. The iso-acids have a slightly larger value of *x* than the corresponding normal acids, the cohesion between branched chains being apparently less than that between normal chains containing the same number of carbon atoms. It is interesting to note that *x* is nearly unity for butyric acid at a water-benzene interface. Immersion in benzene appears to eliminate the attraction between the hydrocarbon chains. This conclusion goes far to justify the assumption that molecules of a fatty acid at a benzene-water interface are orientated with their hydrocarbon chains in the benzene phase, while their polar carboxyl groups are in the aqueous phase.

It will be seen that the existing data are sufficiently complete to enable the linear portion of the curves to be drawn with some accuracy. But, unfortunately, the measurements for small values of *F* are insufficient both in accuracy and number to give more than a rough indication of the course of these parts of the curves. Even so, a comparison of each curve with the $pv/RT - p$ curve of a gas such as N₂ or CO₂ at a temperature for which *x* is the same, shows that the least value observed for FA/RT is consistently larger than the corresponding value of pv/RT . From Table V it is evident that the more elongated the molecule the greater the difference.

* We hope to investigate more fully the properties of such films, and give a more detailed comparison between soluble and insoluble films in a future communication.

Table V.

Substance.	x .	Least value of FA/RT .	Least value of pv/RT .	Difference.
<i>n</i> -Butyric acid	0.73	no minimum	0.98	>0.02
<i>n</i> -Valeric acid	0.63	1.00	0.89	0.11
<i>n</i> -Caproic acid	0.43	0.95	0.62	0.33
Iso-Butyric acid	0.78	1.00	1.00	0.00
Iso-Valeric acid	0.68	0.98	0.95	0.03
Iso-Caproic acid	0.48	0.89	0.74	0.15

It thus appears that the elongated molecules are vertically orientated when close-packed, but their long axes may become considerably inclined to the plane of the interface when in the act of separating one from another. From the data in Table II alone it is impossible to derive any information about the orientation of molecules when completely separated from one another.*

§ 6. *A New Relation between F and C, and the Determination of B and x when only a few Observations are Available.*

Equation (xiii) leads to a new relation between F and C, for on elimination of A by means of Gibbs' equation

$$A = 2.303 RTd \log_{10} \gamma C / dF,$$

and integrating we obtain

$$\log_{10} \gamma C + \text{const.} = x \log_{10} F + \frac{B}{2.303 RT} F.$$

It is sometimes convenient to express this equation in the following form

$$\Delta \log_{10} \gamma C = x \Delta \log_{10} F + \frac{B}{2.303 RT} \Delta F$$

whence

$$\frac{\Delta \log_{10} \gamma C}{\Delta \log_{10} F} = \frac{B}{RT} \cdot \frac{\Delta F}{2.303 \Delta \log_{10} F} + x.$$

Comparing this with equation (xi) and equation (xiii) it is evident that the term $\frac{\Delta F}{2.303 \Delta \log_{10} F}$ is the value of F for which $\frac{\Delta \log_{10} \gamma C}{\Delta \log_{10} F}$ is equal to FA/RT (over the portion of the curve for which equation (xiii) obtains). The mean values of F quoted in Table II have been obtained by this method, and Table VI summarises the data for *n*-valeric acid, columns 1 and 2 being the figures from von Szyszkowski's paper.

* Langmuir, *loc. cit.* (1), p. 1887, considers that Traube's rule gives evidence that adsorbed molecules in this condition lie with their hydrocarbon chains flat on the surface. (See also N. K. Adam, 'Jour. Phys. Chem.,' vol. 29, p. 97 (1925).)

Table VI.—Normal Valeric Acid.

1. C in mols. per litre.	2. $\frac{\sigma}{\sigma_0} \times 10^3$.	3. F dynes/cm. $\sigma_0 = 72.95$.	4. $\Delta \log_{10} C$.	5. $\Delta \log_{10} \gamma$.	6. $\frac{\Delta \log_{10} \gamma C}{\Delta \log_{10} F}$ $= \frac{FA}{RT}$.	7. $\frac{\Delta F}{2.303 \Delta \log_{10} F}$ $= F$ (mean).
0.1995	504	36.19				
0.1333	574.5	31.04	0.1751	0.0002	2.63	33.6
0.0884	642	26.11	0.1789	0.0003	2.39	28.5
0.0589	707	21.38	0.1774	0.0012	2.05	23.6
0.0393	766	17.07	0.1742	0.0016	1.80	19.2
0.0262	823	12.91	0.1761	0.0019	1.50	14.9
0.0175	872	9.34	0.1753	0.0025	1.26	11.0
0.0116	911.5	6.46	0.1765	0.0033	1.12	7.8
0.0078	941	4.30	0.176	0.0040	1.02	5.3
0.0052	961	2.85	0.176	0.0045	1.00	3.5

Thus, by means of a few determinations of the surface tension of solutions values of FA/RT may be obtained with accuracy.

In Table VII the data of Gouy (18) for iso-amyl alcohol at a sodium sulphate solution mercury interface are employed for computing the values of FA/RT

Table VII.—Tertiary Amyl Alcohol Water-Mercury.

1. C in mols. per litre.	2. Capillary Reading.	3. F* dynes/cm.	4. $\frac{\Delta F}{2.303 \Delta \log_{10} F}$ $= F$ (mean).	5. $\frac{\Delta \log_{10} C}{\Delta \log_{10} F}$ $= \frac{FA}{RT}$.
0.0000	1001.7			
0.0125	992	4.14		
0.025	981	8.83	6.54	0.91
0.05	966	15.24	11.76	1.27
0.10	949	22.48	18.59	1.78

* The alcohol was dissolved in normal Na_2SO_4 solution. σ_0 is taken as the maximum surface tension in this solution, not pure water. Columns 1 and 2 from Gouy, ref. (18).

for various values of F . When plotted these points are found to lie on a straight line, and the constants thus derived are given in Table III.

In the case of the adsorption at a mercury-water interface of tertiary amyl alcohol and the more dilute solutions of tertiary butyl alcohol (< 1.0 molar) the laws of ideal solutions are applicable, but for strong solutions similar modifications have to be introduced as in the consideration of adsorption at a water-air interface. Whilst the surface concentrations can in all cases be determined from a knowledge of the activities of the solute, any variations in σ_0 , the surface tension of the solution without the Gibbs' film, will render worthless any values of FA/RT calculated by the above method. This appears to be the case for methyl alcohol, acetone and the stronger solutions of tertiary butyl alcohol. On the other hand Gouy (19) has determined the mercury-water interfacial surface tensions in the presence of cane-sugar, a substance which raises the surface tension at a water-air interface 2.0 dynes per centimetre for 0.8 molar (20), and is thus unlikely to cause serious alterations in σ_0 even in strong solutions. It is satisfactory to find in this case also that the equation (xiii) is applicable.

For computation of the activities the osmotic pressures (21) have been employed. The data so obtained are shown in Table VIII, from which the curves in fig. 5 have been made. The difference between the linear character of the continuous curve determined with the aid of the osmotic pressure data, and the dotted curve computed on the assumption that the solutions are ideal, is striking. It will be noted that the value of x for cane-sugar is unity, as is also the case for the corresponding term in the osmotic pressure expression

$$P(v - b) = x RT \quad (22).$$

We should anticipate that the length of a sucrose molecule consisting of two molecules of hexose sugars joined by an oxygen atom would slightly exceed $12 \times 1.33 = 16.0$ Å.U., 1.33 Å.U. being the distance which separates carbon atoms along the axis of a hydrocarbon chain (found by Adam). According to the same author the area occupied by a H_2COH group is 21.6 Å.U. Hence, the thickness of a hexose chain which consists of $HCOH$ groups is probably a little less than 4.66 Å.U. If, therefore, an adsorbed sucrose molecule has its long axis in the plane of the interface, a value for B of about $4.66 \times 16.0 = 74.6$ Å.U. is to be expected. The agreement between this and 72.7 found experimentally for B is satisfactory, and indicates that our assumption about the orientation of the molecule is correct.

Table VIII.—Cane-Sugar—Water-Mercury 18° C.

1. C in mols. per litre.	2. P* — RTC	3. Capillary Reading.†	4. F dynes/ cm.	5. $\frac{\Delta F}{2 \cdot 303 \Delta \log_{10} F}$	6. $\frac{\Delta \log_{10} P}{\Delta \log_{10} F}$	7. $\frac{\Delta \log_{10} C}{\Delta \log_{10} F}$
0.000		1000.0				
0.010	1.00	988.6	4.86			
0.100	1.03	971.1	12.33	8.0	2.51	2.48
0.333	1.15	959.2	17.42	14.8	3.72	3.49
1.000	1.50	945.3	23.34	20.2	4.74	3.75
2.000	2.35	933.1	28.54	25.6	5.63	3.39

* From data of Earl of Berkeley and Hartley at 0° C. (21). A comparison with data of Morse and Frazer (which do not extend over sufficient range) shows that P/RTC at a given volume concentration is practically independent of temperature.

† Columns 1 and 3 from Gouy, ref. (19).

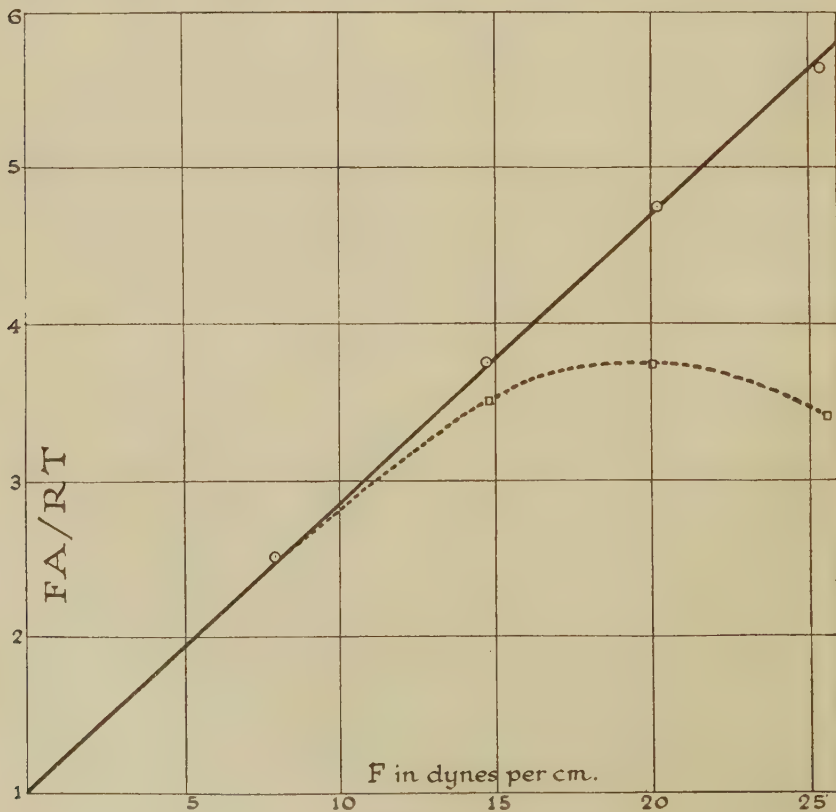


FIG. 5.

§ 7. *A Determination of the Pressures to which One Dyne per Centimetre Corresponds.*

It is interesting to compute the pressure to which a definite value of F is equivalent. Adam (23) has suggested that this may be evaluated by consideration of the thickness of the Gibbs' layer, over which the force F operates, or the equivalent pressure as given by the equation

$$p = F/\delta,$$

where δ is the thickness of Gibbs' layer, *i.e.*, the length of an orientated molecule.

On the kinetic hypothesis it is evident that this method of computation is invalid, for the pressure on a molecule cannot be regarded as a uniform thrust over its whole length, but as due to successive impacts between it and its neighbours, regardless of its length. For an accurate evaluation of this pressure we must compare the surface phase with a bulk phase in the same condition, *i.e.*, showing the same value of x . Such comparison is possible between cane sugar adsorbed at a mercury-water interface and sugar in aqueous solution, for in both cases $x = 1$. For an aqueous solution (at 0°C.) showing an osmotic pressure of one hundred atmospheres, $Pv/RT = 2.3$, whilst FA/RT has this value for the surface phase when $F = 6.8$ dynes per centimetre (at 18°C.). Thus, 6.8 dynes per centimetre is equivalent to a pressure of 100 atmospheres or 1 dyne per centimetre is equivalent to 14.7 atmospheres.

Again, from a comparison of the equations

$$\frac{FA}{RT} = \frac{B}{RT} \cdot F + x$$

and

$$\frac{pv}{RT} = \frac{b}{RT} \cdot p + x,$$

it is clear that for identical values of x $FA/RT = pv/RT$ when $p/F = B/b$. Thus, the pressures corresponding to F may be determined from the value of b for a gas which gives value of x identical with that of the substance under examination. For nitrogen at 0°C. x in Amagat's equation is equal to 0.73 for a range of pressure 400 to 1,500 atmospheres; this is identical with the value for normal butyric acid at the water-air interface at 19°C. b for nitrogen is 30.5 c.c. per gram mol., and B for butyric acid is 1.47×10^9 sq. cm. per gram mol.

$$\therefore \quad \frac{p}{F} = \frac{1.47 \times 10^9}{30.5} = 4.82 \times 10^7.$$

Hence, 1 dyne per centimetre is equivalent to a pressure 4.82×10^7 dynes per sq. cm., or 47.7 atmospheres.

Summary.

The surface tension---concentration curves for aqueous solution of a number of capillary active organic substances have been examined. Provided that Gibbs' equation be applied in its correct form, evidence is obtained in the case of dilute solutions in support of the unimolecular character of the adsorbed film.

The analogy between the lowering, F , of the surface tension, and a three-dimensional gas or osmotic pressure postulated by Traube has been critically examined. For weak solutions when F exceeds some 10 dynes per centimetre, the surface phase is relatively highly condensed and the equation $F(A - B) = xRT$, analogous to that of Amagat connecting the pressure and volume of highly compressed gases, is obeyed. In this equation A is the area occupied by a gram. mol. of the active substance at the interface, B is the limiting area of a gram. mol. under high compression, and $1/x$ is a measure of the lateral molecular cohesion. The relation has been tested at three interfaces, viz., water-air, water-benzene, and water-mercury.

This equation, which rests on a theoretical basis and is for this reason to be preferred to the empirical equations of Milner or von Szyszkowski, fits the existing data within the limits of experimental error, which the older ones do not.

It yields values of the limiting areas of the adsorbed molecules in very close agreement with those anticipated from our knowledge of molecular dimensions. At interfaces between water and air and water and benzene the common value of B 24-25 Å.U. found for normal fatty acids supports Langmuir's orientation hypothesis.

The values of x for a series of fatty acids show that at a water-air interface the lateral molecular cohesion increases with the length of the hydrocarbon chain. There is little or no cohesion between such molecules at a water-benzene interface. Sucrose molecules do not cohere at a water-mercury interface; this is interesting, as the same conclusion has been drawn about their behaviour in the body of an aqueous solution.

These and other facts afford strong grounds for believing that the molecules of the capillary active substances examined are adsorbed from a weak solution in a unimolecular layer, and that the effect they produce on the surface tension is due to their thermal agitation alone. At a given temperature their effectiveness depends solely on their surface concentration, their interfacial areas and their lateral cohesion.

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A Contribution to the Study of the Optical Properties of Mixed Crystals.

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THEORETICAL.

1. *Introduction.*—The optical properties of isomorphous mixtures produced in the laboratory have been studied by various crystallographers since the time of Senarmont, who found that the optic axial angle of mixtures of the potassium- and ammonium-seignette salts was intermediate between those of the simple salts and varied gradually with the composition of the mixtures. Such artificially prepared mixtures offer better material for investigation than do the mixtures occurring as minerals, since their composition is simpler and can be varied at will. The first quantitative results were obtained by Dufet,* who measured

* H. Dufet, 'Bull. Soc. Fr. Min.,' vol. 1, p. 58 (1878).

the mean refractive index (β) of mixtures of the orthorhombic sulphates of magnesium and nickel and enunciated the law: "The differences between the refractive indices of a mixture of two isomorphous salts and those of the component salts are inversely proportional to the numbers of molecules of the two salts in the mixture." This is equivalent to the statement that in (orthorhombic) mixed crystals the refractive index of a mixture is a linear function of its composition as expressed in molecular percentage. Thus, if N n' n'' are the refractive indices of the mixed crystal and of the two components, respectively, and m' m'' are the molecular percentages of the two components

$$N = \frac{m'n' + m''n''}{100}.$$

Mixtures of potassium- and thallium-alum,* of strontium and lead dithionates,† and of magnesium and zinc sulphates‡ were found to obey Dufet's law, though mixtures of magnesium sulphate and magnesium chromate‡ apparently did not do so. In the latter case, however, the deviations may have been due to want of homogeneity in the crystals, as suggested by Dufet.

Mallard§ had previously proposed two different methods by which on the analogy of the phenomena produced by the superposition of thin crystalline plates, the optical properties of a mixed crystal might be calculated from those of its components. These methods are quite general, and applicable to crystals of any system. In the case of orthorhombic substances, the first of these led to the relation:—

$$\begin{aligned}\frac{100}{(N_a)^2} &= \frac{m'}{(n_a')^2} + \frac{m''}{(n_a'')^2}, \\ \frac{100}{(N_b)^2} &= \frac{m'}{(n_b')^2} + \frac{m''}{(n_b'')^2}, \\ \frac{100}{(N_c)^2} &= \frac{m'}{(n_c')^2} + \frac{m''}{(n_c'')^2},\end{aligned}$$

in which N_a , n_a' , n_a'' are the refractive indices of the mixed crystals and of the two components, respectively, for vibrations along the a -axis, and N_b , n_b' , n_b'' , N_c , n_c' , n_c'' are the corresponding indices relating to the b - and c -axes, and m' , m'' are the molecular percentages of the two components.

* A. Fock, 'Zs. Krys.,' vol. 4, p. 583 (1880).

† H. Dufet, 'Bull. Soc. Fr. Min.,' vol. 3, p. 180 (1880).

‡ A. Fock, *loc. cit.*

§ E. Mallard, 'Ann. d. Mines,' 7th Ser., vol. 10, p. 175 (1876).

The second led, in the same case, to the same relation which had been found experimentally by Dufet for the mean index, viz. :—

$$N_a = \frac{m'n_a' + m''n_a''}{100},$$

$$N_b = \frac{m'n_b' + m''n_b''}{100},$$

$$N_c = \frac{m'n_c' + m''n_c''}{100}.$$

Both these formulæ were tested by Mallard* on the original observations of Dufet, as well as on measurements by Wyruboff of the optic axial angle of mixtures of potassium sulphate and ammonium sulphate, and of potassium sulphate and potassium chromate, and both were found to give satisfactory agreement, so far as could be expected with the data then available. It was, however, realised by Mallard, and was proved later by Lavenir, that the two formulæ, though differing from one another, must necessarily give nearly identical results in the cases so far examined, owing to the slight differences between the refractive indices of the components; and in order to distinguish between them Lavenir† made very careful measurements of the indices of mixtures of the potassium- and ammonium-seignette salts.

Lavenir showed (1) that the indices of these mixtures are closely represented by the formulæ :—

$$\left. \begin{aligned} N_a &= k'n_a' + k''n_a'' \\ N_b &= k'n_b' + k''n_b'' \\ N_c &= k'n_c' + k''n_c'' \end{aligned} \right\} \text{ where } k' + k'' = 1,$$

i.e., that the refractive index of a mixture for vibrations along any one of its axes is a linear function of the corresponding indices of the two components, this function being the same for all three axes, and (2) that the coefficients k' k'' are proportional to the molecular percentages, as stated by Dufet. The results obtained by Lavenir were thus in favour of the second formula of Mallard, of which Dufet's law forms a special case, applying to crystals in which the principal vibration-directions are coincident in the two components.

Mallard's second formula was applied by himself‡ to the general case of the anorthic feldspars, and the results were found to agree well with those obtained by Max Schuster.

* E. Mallard, 'Bull. Soc. Fr. Min.,' vol. 3, p. 3 (1880), and vol. 4, p. 71 (1881).

† A. Lavenir, 'Bull. Soc. Fr. Min.,' vol. 17, p. 153 (1894).

‡ E. Mallard, 'Bull. Soc. Fr. Min.,' vol. 4, p. 96 (1881).

Doubt was afterwards thrown upon the nature of the coefficients k' k'' of Lavenir's formulæ by G. Wulff,* who suggested that they might rather represent the proportions by *volume* of the components.

Dufet had found that his law, which had been arrived at empirically, was deducible from the law of Gladstone on the refractive power of mixtures, on the assumption that the densities of isomorphous salts are proportional to their molecular weights. Wulff† pointed out, however, that this is incorrect, since it would imply equality in their molecular volumes, and showed that Gladstone's law would require that the composition of the mixture should be expressed in percentage by volume instead of in molecular percentage. In most cases of isomorphous mixture the difference is but slight, since similarity of molecular volume is a necessary condition for the formation of homogeneous mixtures.

In order to determine the nature of the coefficients k' k'' , Wulff examined (monoclinic) mixtures of ammonium-magnesium and cæsium-magnesium sulphates, which differ considerably in their densities and molecular weights; and from a comparison of the observed extinction angles of mixtures of known composition with those calculated by Mallard's method from the constants of the components he concluded that the refractive indices of the mixtures vary in proportion to their composition by *volume*.

Later, however, Wulff felt that his previous work, while showing that k' k'' represented the composition by volume rather than by weight, was not conclusive as between the former and molecular percentage, owing to the slight difference between the molecular volumes of the components. He, therefore, examined mixtures of potassium and ammonium sulphates, of which the density, molecular weight and molecular volume are all sufficiently different to give a prospect of deciding the question. In this case he determined the double refraction of the mixtures, *i.e.*, the differences between their indices, which, if Lavenir's equations are true, must be related to the composition in the same way as are the refractive indices:—

$$N_a - N_b = k' (n_a' - n_b') + k'' (n_a'' - n_b''),$$

etc.

The results were found to be directly opposed to the previous evidence, the double refraction appearing to vary in proportion to the composition by *weight*. As, however, this might have been due to a want of homogeneity

* G. Wulff, 'Zs. Krys.,' vol. 36, p. 1 (1902).

† G. Wulff, 'Zs. Krys.,' vol. 42, p. 558 (1907).

in the mixed crystals, caused by the somewhat considerable difference in the molecular volumes, Wulff attempted a crucial test on mixtures of ammonium and rubidium sulphates, of which the molecular volumes are nearly equal, and which gave clear and well-formed mixed crystals. In this case the double refraction was found not to vary proportionally to the composition, whether this were expressed in terms of weight, of volume, or of number of molecules. From his results, Wulff drew the final conclusion that in isomorphous mixed crystals there exists *no* linear relation between the principal refractive indices of the mixtures and those of the components.

It may be noticed, however, that these conclusions are based, not upon direct measurements of the refractive indices, but upon measurements of the double refraction, *i.e.*, the difference between two indices—an extremely small quantity, and one of which the measurements quoted appear to have varied within somewhat wide limits.

In view of the divergence between Wulff's results and those obtained by most previous observers, it seemed desirable to pursue the matter further, and to determine directly the refractive indices of the mixed crystals. The present paper relates to certain mixtures of the well-known monoclinic series of double sulphates and chromates of magnesium and alkalis.

EXPERIMENTAL.

Part I.—*Ammonium-magnesium Sulphate and Ammonium-magnesium Chromate.*

1. *Selection of Material.*—A number of trial mixtures of various pairs of isomorphous monoclinic salts were prepared before two were found which seemed likely to fulfil the object of this research. It was found necessary to take the following considerations into account. It is essential that the salts shall mix in all proportions and form homogeneous mixed crystals of sufficient size and with suitable surfaces for work with the Abbe refractometer. For this purpose the pair of isomorphous salts must possess close molecular volumes. The mixtures should also admit of accurate analysis by simple chemical methods; or, alternatively, they must possess densities so far apart that the composition of a mixture can be estimated from a determination of its density. Limitations were also found in the optical character of the salts. Thus, ammonium*-zinc and rubidium†-zinc sulphates are unsuitable, for although they have close molecular volumes (206·4 and 205·6), their refractive indices are too nearly

* A. E. H. Tutton, 'Journ. Chem. Soc.,' vol. 87, p. 1123 (1905).

† A. E. H. Tutton, 'Journ. Chem. Soc.,' vol. 69, p. 379 (1896).

equal. There is, for example, a difference of only 0.004 in the values for β , and a change of 1 per cent. in the composition of the mixed crystals would thus correspond to a change of only about 0.00004 in the refractive index.

Certain other members of the same series, however, seemed to show sufficient difference in optical properties to encourage investigation: for example, ammonium-magnesium sulphate* and ammonium-magnesium chromate.† In both these salts the optic axial plane is parallel to the plane of symmetry, but in the first the positive acute bisectrix emerges obliquely through $a(100)$, and in the other it emerges obliquely through $c(001)$. The refractive indices for sodium light are as follows:—

Ammonium-magnesium Sulphate. Ammonium-magnesium Chromate.

$$\alpha = 1.4716$$

$$\beta = 1.4730$$

$$\gamma = 1.4786$$

$$\alpha = 1.6363$$

$$\beta = 1.6371$$

$$\gamma = 1.6531$$

There is here a considerable difference in the values of the refractive indices, and this pair was selected for the first measurements. The molecular volumes of the salts are respectively 207.8 and 216.9.

2. *Preparation of Mixed Crystals.*—Mixed crystals of the two salts were made in varying proportions from 0 per cent. to 100 per cent. by weight of sulphate. Ammonium chromate is somewhat unstable, and apt on heating to lose ammonia, with the formation of bichromate; precautions were therefore taken against any prolonged heating of the solution. To avoid the possibility of any extensive variation in the composition of the crystals separated, only small crops, weighing from 1 to $3\frac{1}{2}$ grams, were allowed to crystallize from a solution containing about 40 grams of salts. Some 17 mixtures were analysed, and the relation between the proportions of the two substances in the solution and in the mixed crystals deposited was determined. The nature of this relation is shown by the accompanying curve (fig. 1), the ordinates expressing the percentage by weight of sulphate in the crystals, and the abscissæ the corresponding percentage in the solution.‡ As a result of this work it became possible to prepare mixed crystals of any desired composition.

* A. E. H. Tutton, 'Journ. Chem. Soc.,' vol. 87, p. 1123 (1905).

† A. E. H. Tutton and M. W. Porter, 'Min. Mag.,' vol. 16, p. 169 (1912).

‡ It may be mentioned that Fock worked out the corresponding curve for mixtures of copper-ammonium sulphate and nickel-ammonium sulphate (A. Fock, 'Zs. Krys.,' vol. 28, p. 337, 1897). The result was a curve very similar in outline to the one here described.

3. *Method of Analysis*.—A volumetric method of analysis based on the oxidation by the chromate of an acidified solution of potassium iodide was

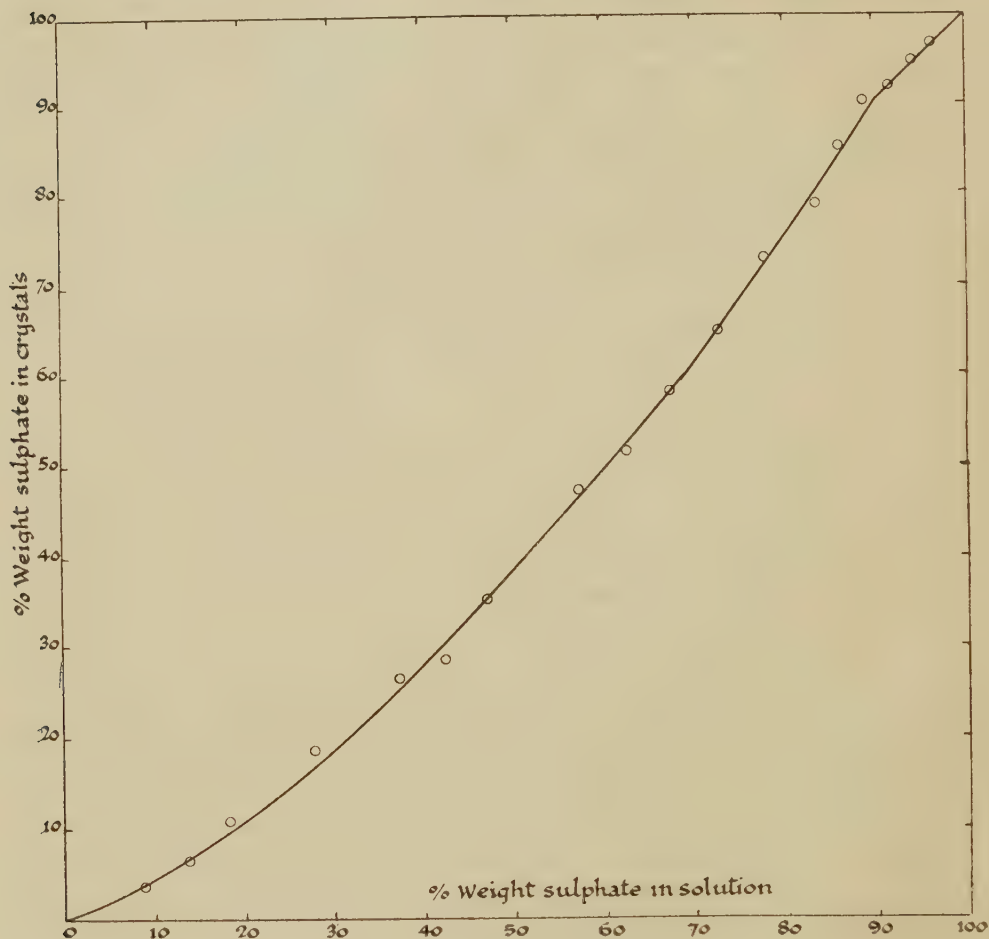
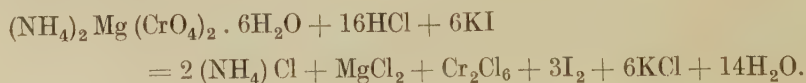


FIG. 1.

employed. The estimation of the iodine so liberated was carried out by the well-known thiosulphate method. The reaction is as follows :—



4. *Goniometrical Measurement of Crystals*.—The measurement of seven different mixtures, including 24 crystals, was carried out on the Goldschmidt two-circle goniometer, as also the measurement of four crystals each of the pure double salts, and the following table gives a means of comparing the axial

ratios and the prism angle of the different mixtures. In no case did the mixtures give crystals as good as those of the pure salts. The faces of $c(001)$ were invariably striated parallel to the plane of symmetry, and for this reason gave a band of images. It will be noted that the value of the axial ratio $a:b$ decreases gradually in passing from the pure sulphate to the pure chromate; the values of the ratio $c:b$ of the pure salts are so nearly identical that the variations of this ratio are practically within experimental errors.

Crystallographic Constants and Prism Angles of Ammonium-magnesium Sulphate, Ammonium-magnesium Chromate, and their Mixtures.

Percentage of Sulphate by Volume.	Number of Crystals Measured.	Axial Ratios $a:b:c$	β	Prism Angle $p \wedge p$	Notes on Crystals.
0.00	3	0.7517 : 1 : 0.4935	106 07	71 40	Excellent.
14.51	3	0.7499 : 1 : 0.4935	106 15	71 30	Fair.
22.91	4	0.7485 : 1 : 0.4942	106 13	71 24	Poor.
43.85	3	0.7476 : 1 : 0.4928	106 32	71 16	Poor.
66.66	4	0.7472 : 1 : 0.4910	106 39	71 12	Fair.
72.52	4	0.7451 : 1 : 0.4930	106 55	70 58	Fair.
84.22	3	0.7440 : 1 : 0.4917	106 54	70 54	Good.
92.94	3	0.7437 : 1 : 0.4935	107 00	70 50	Fair.
100.00	4	0.7409 : 1 : 0.4924	107 06	70 35	Excellent

5. *General Optical Scheme.*—The examination of the optical properties was carried out in sodium light under the polarising microscope. The general optical properties of the pure salts must first be recalled.* In both salts the optic axial plane is the plane of symmetry, in other respects there are differences. In the sulphate (fig. 10) the positive acute bisectrix is inclined at $94^\circ 58'$ to the vertical axis- c , and at $12^\circ 8'$ to the a -axis; the observed axial angle $2E$ for sodium light is $79^\circ 11'$. In the chromate, on the other hand (fig. 2), the positive acute bisectrix lies $12^\circ 40'$ behind the normal to $c(001)$, and $3^\circ 27'$ in front of the vertical axis- c . The observed axial angle $2E$ for sodium light is $45^\circ 8'$.

In mixtures containing from 0 to 10 per cent. by volume of sulphate the optic axial plane is the symmetry plane $b(010)$; the acute bisectrix (γ) emerges through $c(001)$, as shown in fig. 2, and the axial angle gradually diminishes as the composition approaches 10 per cent. Somewhere between this and 14 per cent. of sulphate the two smaller indices α and β become equal and the mixtures are uniaxial (fig. 3). The axes now open out in a plane perpendicular

* See Tutton, *loc. cit.*

to the symmetry plane, as shown in fig. 4. The axial angle gradually increases, and between 58 and 67 per cent. the symmetry axis- b becomes the acute bisectrix (fig. 5) and the double refraction is negative.

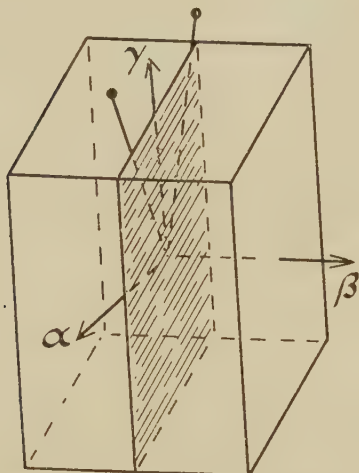


FIG. 2.—0–10 per cent. of sulphate by volume.

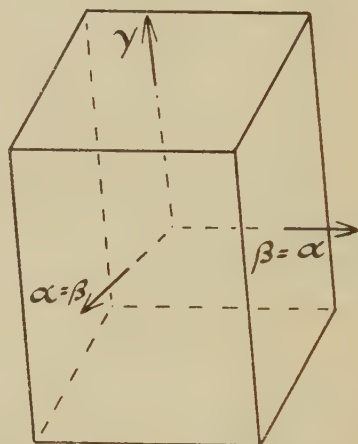


FIG. 3.—10–14 per cent. of sulphate by volume.

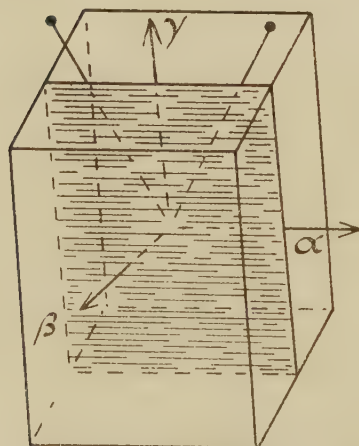


FIG. 4.—14–58 per cent. of sulphate by volume.

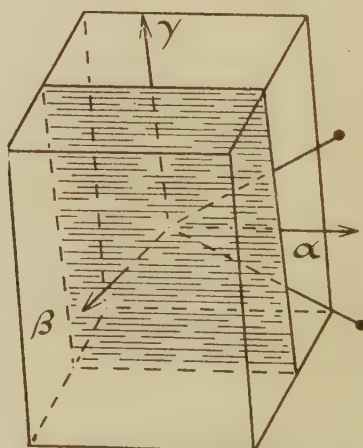


FIG. 5.—58–67 per cent. sulphate by volume.

Hitherto the variation in axial angle has been gradual but now the change becomes remarkably rapid. Between 67 and 72 per cent. of sulphate β and γ become equal and the crystals are uniaxial (fig. 6), and beyond 72 per cent. the axes open out in the perpendicular plane, the symmetry axis- b still being the

acute bisectrix (fig. 7). The axial angle now rapidly increases through 90° until the positive acute bisectrix emerges obliquely through $a(100)$ (fig. 8) in the mixtures examined between 84 and 89 per cent. Between 89 and 93

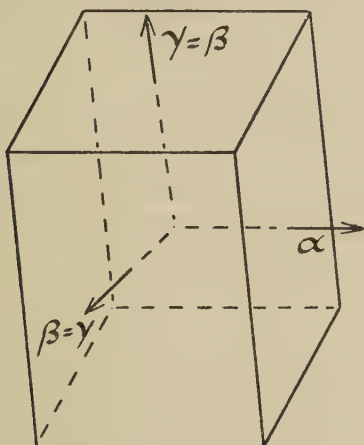


FIG. 6.—67–72 per cent. sulphate by volume.

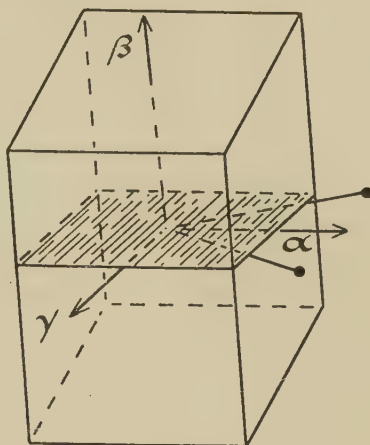


FIG. 7.—72–84 per cent. sulphate by volume.

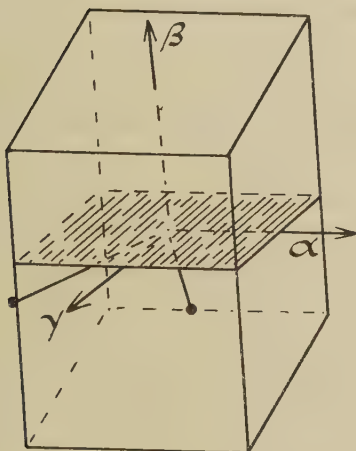


FIG. 8.—84–89 per cent. sulphate by volume.

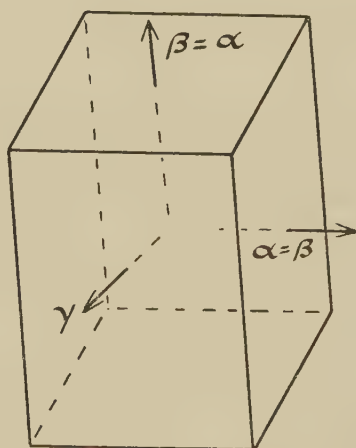


FIG. 9.—89–93 per cent. sulphate by volume.

per cent. the smaller indices again become equal (fig. 9). Between 93 and 100 per cent. of sulphate the axial plane is the symmetry plane $b(010)$ (fig. 10), and the axial angle gradually increases until with 100 per cent. of sulphate $2E$ is equal to $79^\circ 11'$.

6. *Optical Anomalies.*—The examination of the mixed crystals revealed the

fact that most of them were not homogeneous. This is proved by the occurrence of optical anomalies, which need only be briefly mentioned here, and which

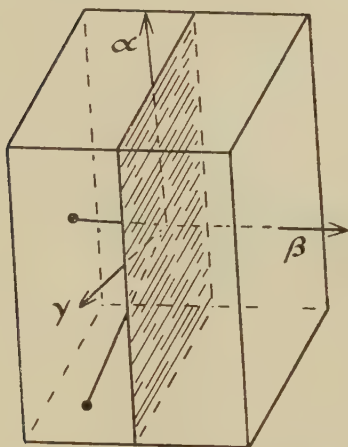


FIG. 10.—93–100 per cent. sulphate by volume.

were noted throughout the series of mixtures, from 4 to 98 per cent. of sulphate. The lack of homogeneity was shown by the following properties:—

(1) Variable extinction on different parts of the face $c(001)$.

(2) Division of faces $b(010)$ into sectors showing extinction angles which were unequal in adjacent pairs of sectors, but equal in opposite pairs.

(3) Banding on $c(001)$ parallel to the plane of symmetry (somewhat resembling the twin banding of feldspars). In convergent light distorted interference figures were noted, with their axial planes neither in the plane of symmetry nor at right angles to it.

7. *Refractive Indices*.—An Abbe refractometer with glass hemisphere, made by Zeiss,* was employed for the determination of the refractive indices, sodium light being used throughout. Unfortunately, owing to the lack of homogeneity already mentioned, the limits in the field of the refractometer were in places confused or even invisible, and the determination of the indices with an accuracy of three or four in the fourth decimal place was found to be impossible. In some cases the values obtained from different forms on one and the same crystal were not in agreement. The mean results are given in the following table.

Refractive Indices of Mixed Crystals of Ammonium Magnesium Sulphate and Ammonium Magnesium Chromate.

Percentage of Sulphate by Volume.	α	β	γ
11.60	1.627	1.627	1.641
37.21	1.589	1.590	1.598
56.24	1.554	1.557	1.560
73.79	1.520	1.525	1.528
89.99	1.491	1.493	1.495
98.04	1.475	1.476	1.482

* C. Pulfrich, 'Zs. Krys.,' vol. 30, p. 574 (1899).

The results were plotted using the composition expressed in proportions by weight, by volume, and by number of molecules, respectively as abscissæ. No proportionality was noted between the refractive indices and the composition of the mixed crystals, however expressed; but owing to the lack of homogeneity of the crystals it is unsafe to draw any conclusions from the results, and it was therefore decided to examine other pairs of salts with a view to obtaining homogeneous mixed crystals.

Mixtures of ammonium-magnesium chromate and selenate, of which the molecular volumes (216.9 and 219.4 respectively) are more nearly equal, were next tried. In these optical anomalies were much less marked than in the former mixtures, but the crystals were still not sufficiently homogeneous to yield reliable results.

Ammonium-magnesium and rubidium-magnesium chromates, of which the molecular volumes are still more nearly equal, were therefore finally chosen.

Part II.—*Ammonium-Magnesium Chromate and Rubidium-Magnesium Chromate.*

1. *Properties of the Pure Salts.*—These salts have molecular volumes 216.9 and 215.5 and were found to mix in all proportions, forming homogeneous mixed crystals of a small size, but with good surfaces. Their densities were found to be as follows:—

Ammonium-magnesium chromate = 1.835

Rubidium-magnesium chromate = 2.463

Difference 0.628

The density thus offered a ready method of determining the relative proportion of each salt present in a mixture, for a change of 1 per cent. in composition corresponds to a density difference of 0.00628.

The optics of ammonium-magnesium chromate have already been mentioned (p. 85), and it is sufficient to repeat that the optic axial plane of this salt is the plane of symmetry b (010), and that the positive acute bisectrix lies $3^\circ 27'$ in front of the vertical axis c , and that the observed optic axial angle $2E$ for sodium light is $45^\circ 8'$ (fig. 15).

The optic axial plane of the rubidium salt,* on the other hand, is perpendicular to the plane of symmetry, and the negative acute bisectrix is the symmetry axis b ; the obtuse bisectrix (γ) lies $48^\circ 10'$ behind the vertical axis c and nearly parallel to the normal to r' ($\bar{2}01$) (fig. 12).

* Tutton and M. W. Porter, 'Min. Mag.', vol. 16, p. 169 (1912).

The optic axial angle for sodium light is too large to be measurable in air. The refractive indices of the two salts for sodium light are as follows :—

Ammonium-magnesium Chromate.

$$\alpha = 1.6363$$

$$\beta = 1.6371$$

$$\gamma = 1.6531$$

Rubidium-magnesium Chromate.

$$\alpha = 1.6217$$

$$\beta = 1.6330$$

$$\gamma = 1.6435$$

There is a fair difference here in the values of the refractive indices. The double refraction is strong throughout the series of mixtures, and it is important to note that the intermediate index remains apart from the two others, except close to the single uniaxial point at the ammonium end of the series, thus avoiding any difficulty in fixing the limits in the field of the refractometer. Optical anomalies appear near the uniaxial point only, and are slight.

2. *Preparation of Mixed Crystals.*—Mixed crystals were made with varying proportions from 0 to 100 per cent. of ammonium-magnesium chromate. Small crops weighing from 5 to 10 grammes were crystallized out of a solution containing about 30 grammes of salts.

3. *Relative Proportions of the Two Double Salts in the Mixtures.*—Owing to the considerable difference between the densities of the two salts, Retgers' method suggested itself as the most convenient means of determining the relative proportion of the two salts in any mixture by means of its density. The equilibrium relations of the aqueous solution were determined and are given in fig. 11, in which the ordinates represent the percentages of ammonium-magnesium chromate by weight in the solution, whilst the abscissæ give the percentages of the same salt in the mixed crystals as determined by Retgers' method. In this case the curve approximates to a straight line at 45° to the axes, showing that the composition of the crystals separated is nearly the same as that of the solution.

This will be of considerable importance for the formation of homogeneous mixed crystals, since the composition of the solution will not be affected by the separation of crystals. This pair thus differs from the pair previously described (as also the pair ammonium-magnesium chromate and selenate), where there is a considerable divergence between the proportions of the two salts in the solution and in the crystals deposited.

The determination of the densities of the two pure salts and of ten of their mixtures was carried out by means of the Westphal balance, using methylene

iodide as the heavy liquid and diluting with benzene.* About twelve determinations have been made for each mixture, the individual crystals always being

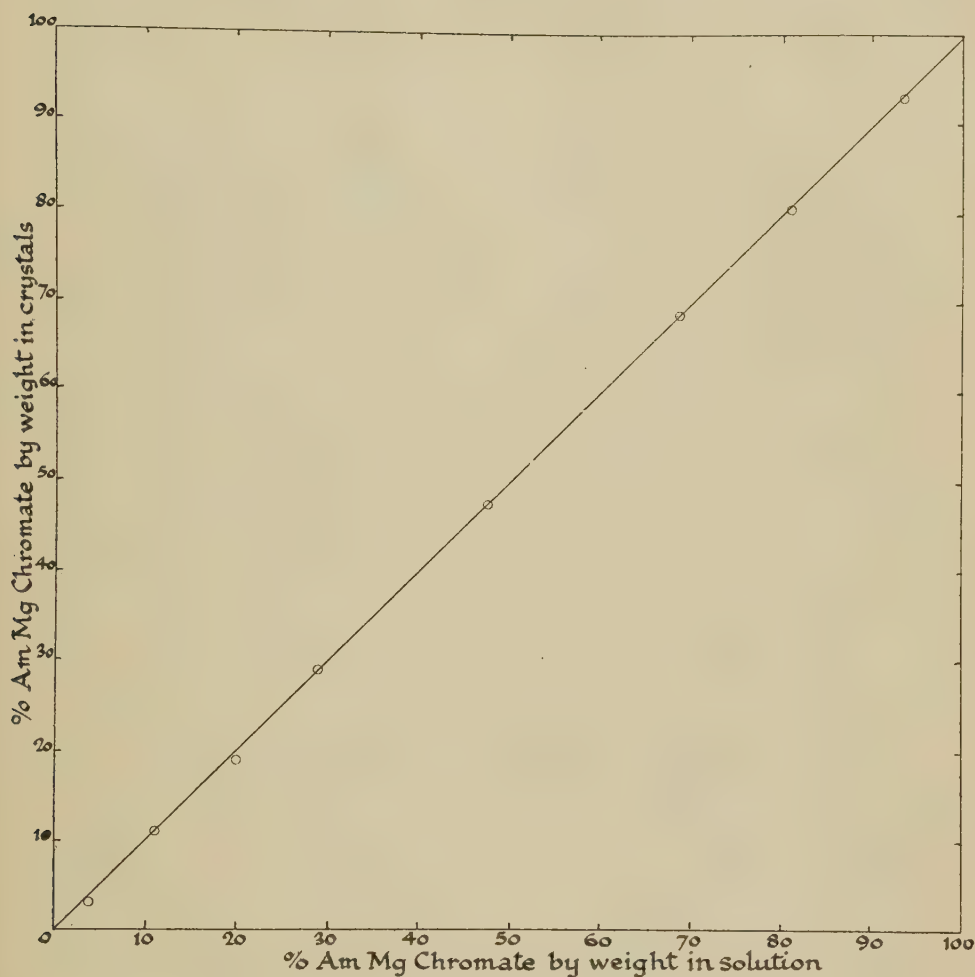


FIG. 11.

selected from the crop actually used for crystal measurement and for the determination of the refractive indices. The mean of the determinations was taken as the final value.

* The temperature of the laboratory on most days was about 16°C ., with the outside limits of $13\frac{1}{2}^{\circ}$ – 18°C .

Densities.

Limits.	Mean.	Percentage of ammonium-magnesium chromate.	
		By Volume.	By Weight.
2.461-2.465	2.463	0.00	0.00
2.435-2.439	2.437	4.14	3.12
2.367-2.379	2.374	14.17	10.95
2.307-2.317	2.313	23.88	18.95
2.238-2.247	2.241	35.35	28.95
2.170-2.179	2.174	46.02	38.85
2.117-2.128	2.122	54.30	46.95
2.077-2.082	2.080	61.00	53.80
1.993-2.003	1.998	74.05	68.03
1.928-1.935	1.932	84.50	80.24
1.867-1.871	1.869	94.58	92.86
1.834-1.836	1.835	100.00	100.00

4. *Goniometrical Measurement of Crystals.*—Four crystals of each of the pure double salts and 49 belonging to the mixtures were measured, and the following table gives a means of comparing the axial ratios and the prism angles of the different mixtures. It must be added here that in no case did the mixtures give crystals as good as those of the pure salts, and also that the faces of c (001) were invariably striated parallel to the plane of symmetry, and for this reason gave a band of images.

Crystallographic constants and prism angles of ammonium-magnesium chromate, rubidium-magnesium chromate and their mixtures.

Percentage of ammonium salt by volume.	Number of Crystals.	$a : b : c$	β	$p \wedge p$	Notes on Crystals.
0.00	4	0.7540 : 1 : 0.4960	104 52	72 10	Excellent.
4.14	5	0.7549 : 1 : 0.4957	105 00	72 12	Fair.
14.17	5	0.7535 : 1 : 0.4968	105 02	72 06	Fair.
23.88	4	0.7554 : 1 : 0.4942	105 12	72 06	Bad.
35.35	5	0.7526 : 1 : 0.4928	105 23	71 56	Fair.
46.02	5	0.7526 : 1 : 0.4942	105 28	71 54	Fair.
54.30	5	0.7517 : 1 : 0.4942	105 34	71 50	Fair.
61.00	5	0.7513 : 1 : 0.4950	105 38	71 46	Good.
74.05	5	0.7522 : 1 : 0.4931	105 47	71 46	Good.
84.50	5	0.7527 : 1 : 0.4950	105 56	71 48	Fair.
94.58	5	0.7508 : 1 : 0.4935	106 04	71 38	Good.
100.00	4	0.7517 : 1 : 0.4935	106 09	71 40	Excellent.

5. *Notes on the Optics of the Mixtures.*—The general scheme of each mixture was studied under the polarising microscope in sodium light. The optic

axial plane of mixtures with from 0 per cent. to 18 per cent. (by volume) ammonium-magnesium chromate is approximately the same as that of the pure rubidium salt, that is perpendicular to the plane of symmetry with an

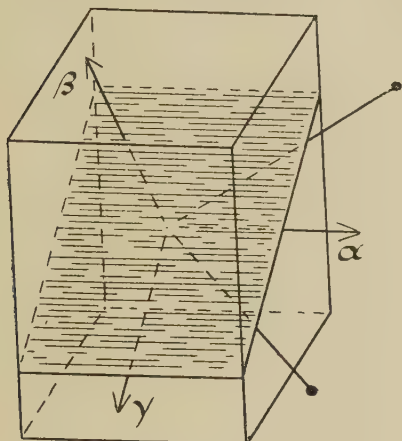


FIG. 12.—0-19 per cent. ammonium salt by volume.

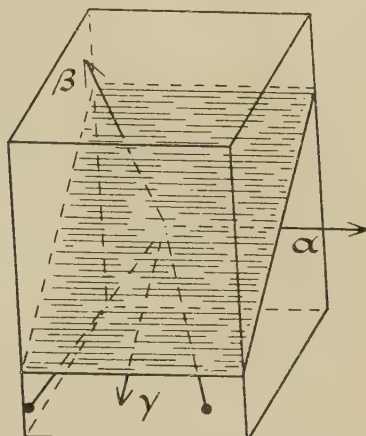


FIG. 13.—19-94 per cent. ammonium salt by volume.

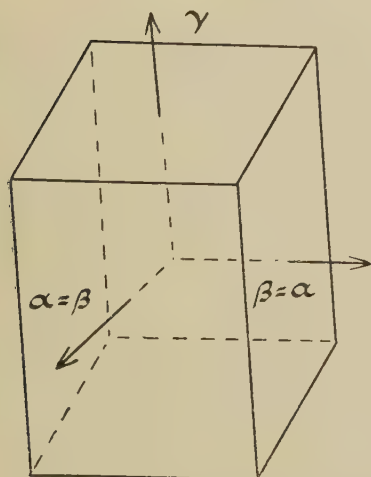


FIG. 14.—95 per cent. ammonium salt by volume.

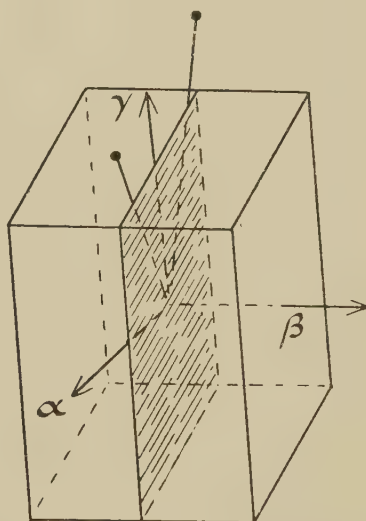


FIG. 15.—95-100 per cent. ammonium salt by volume.

inclination of 48° to the vertical and a gradually increasing optic axial angle about the negative bisectrix (fig. 12). Above 19 per cent. the symmetry axis b is no longer the acute bisectrix and the crystals are optically positive (fig. 13). The optic axial angle now steadily diminishes,

closing up about the positive acute bisectrix until at about 95 per cent. of the ammonium salt α equals β for sodium light and the crystals are uniaxial. Simultaneously the plane of the optic axes gradually inclines forward about the symmetry axis, until at 95 per cent. the axis γ lies slightly in front of the vertical (fig. 14). The extinction angle ($= c' : \gamma$) on b (010) thus gradually changes from $+48^\circ$ in the rubidium to $-3\frac{1}{2}^\circ$ in the ammonium salt. Between 95 and 100 per cent. (fig. 15) the optic axes open out in the plane of symmetry with a gradually increasing optic axial angle.

In crystals with less than 95 per cent. of ammonium-magnesium sulphate no optical anomalies were observed. Crystals of this composition, however, when examined through a natural pair of faces c (001) showed, instead of a single interference figure lying in the plane of symmetry or at right angles to it, as required by monoclinic symmetry, a number of narrow-angled biaxial figures, which were not in the plane of symmetry or at right angles to it, and were differently orientated in different parts of the crystal, but this was no doubt attributable to strains caused by a slight want of homogeneity. It may be pointed out that the crystals of this composition, being uniaxial with rather weak double refraction, will be particularly liable to be thus affected by slight irregular strains.

6. *Refractive Indices of the Pure Salts and of Ten Mixtures.*—The determination of the refractive indices was carried out in sodium light by means of the Abbe refractometer. The crystals were small, with an average size of 3 mm. $\times$ 3 mm. $\times$ 3 mm. Natural surfaces gave better results than polished ones. As a rule four crystals of each mixture were used, and determinations were made on different forms in order to eliminate the fourth false index obtained on the refractometer and to identify β . The average temperature of the laboratory on most days was 15° – 16° C., with the outside limits of 13° – 18° C. Dr. Tutton* found in experiments with ammonium- and rubidium-magnesium chromates that a rise of temperature to 80° from the ordinary temperature only caused a change of about 0.002 in the refractive indices. The slight variation of temperature during the experiments may therefore be neglected.

The following tables give the refractive indices in detail :—

* Tutton, *loc. cit.*

Refractive Indices of Ammonium-Magnesium Chromate, Rubidium-Magnesium Chromate and their Mixtures.

Percentage of ammonium-magnesium chromate by volume.	Form.	α .	β .	γ .
0.00	<i>c</i> (001)	1.6217	1.6330	1.6444
	<i>p</i> (110)	1.6215	1.6330	1.6437
	<i>p</i> (110)	1.6215	1.6329	1.6435
	Mean*	1.6216	1.6330	1.6439
4.14	<i>p</i> (110)	1.6226	1.6333	1.6437
	<i>c</i> (001)	1.6226	—†	1.6444
	<i>q</i> (011)	1.6226	1.6338	1.6437
	<i>p</i> (110)	1.6226	1.6338	1.6436
	Mean	1.6226	1.6336	1.6438
14.17	<i>c</i> (001)	1.6241	1.6350	1.6440
	<i>p</i> (110)	1.6241	1.6350	1.6437
	<i>c</i> (001)	1.6237	1.6345	1.6436
	<i>c</i> (001)	1.6239	1.6350	1.6437
	Mean	1.6239	1.6349	1.6437
23.88	<i>c</i> (001)	1.6249	1.6356	1.6440
	<i>p</i> (110)	1.6256	1.6363	1.6442
	<i>p</i> (110)	1.6257	1.6361	1.6444
	<i>p</i> (110)	1.6257	1.6360	1.6442
	Mean	1.6255	1.6360	1.6442
35.35	<i>c</i> (001)	1.6267	1.6366	1.6444
	<i>p</i> (110)	1.6270	1.6366	1.6444
	<i>c</i> (001)	1.6266	1.6366	1.6446
	<i>p</i> (110)	1.6269	1.6366	1.6444
	Mean	1.6268	1.6366	1.6444
46.02	<i>p</i> (110)	1.6283	1.6367‡	1.6455
	<i>p</i> (110)	1.6286	? 1.6368	1.6455
	<i>p</i> (110)	1.6285	1.6371	1.6456
	Mean	1.6285	1.6369	1.6455
54.30	<i>q</i> (011)	1.6298	1.6370	1.6467
	<i>p</i> (110)	1.6304	1.6371	1.6469
	<i>p</i> (110)	1.6304	1.6374	1.6469
	<i>p</i> (110)	1.6306	1.6371	1.6467
	Mean	1.6303	1.6371	1.6468

* Tutton found $\alpha = 1.6217$, $\beta = 1.6330$, $\gamma = 1.6435$.

† The limit here was too faint to be fixed accurately.

‡ No second form with sufficiently good surfaces could be found in order to identify β in this mixture. Of the two intermediate indices determined one fell on the curve with those of the other nine mixtures and is given above, whilst the other did not.

Refractive Indices of Ammonium-Magnesium Chromate, Rubidium-Magnesium Chromate and their Mixtures—*continued*.

Percentage of ammonium-magnesium chromate by volume.	Form.	α .	β .	γ .
61.00	q (011)	1.6308	1.6368	1.6469
	q (011)	1.6307	1.6368	1.6369
	p (110)	1.6313	1.6370	1.6473
	p (110)	1.6311	1.6368	1.6473
	Mean	1.6310	1.6369	1.6471
74.05	p (110)	1.6332	1.6370	1.6496
	p (110)	1.6330	1.6368	1.6494
	q (011)	1.6330	1.6368	1.6492
	p (110)	1.6330	1.6370	1.6489
	Mean	1.6330	1.6368	1.6493
84.50	q (011)	1.6342	1.6363	1.6503
	p (110)	1.6346	1.6368	1.6506
	p (110)	1.6348	1.6370	1.6512
	p (110)	1.6348	1.6367	1.6507
	Mean	1.6346	1.6367	1.6507
94.58	q (011)	1.6363 =	1.6363	1.6520
	p (110)	1.6364 =	1.6364	1.6523
	p (110)	1.6367 =	1.6367	1.6523
	p (110)	1.6366 =	1.6366	1.6520
	Mean	1.6365 =	1.6365	1.6522
100.00	p (110)	1.6363	1.6373	1.6530
	q (011)	1.6360	1.6370	1.6526
	p (110)	1.6366	1.6371	1.6529
	Mean§	1.6363	1.6371	1.6528

§ Tutton found $\alpha = 1.6363$, $\beta = 1.6371$, $\gamma = 1.6531$.

Summary Table of Refractive Indices.

Percentage by volume of ammonium-magnesium chromate.	α .	β .	γ .
0.00	1.6216	1.6330	1.6439
4.14	1.6226	1.6336	1.6438
14.17	1.6239	1.6349	1.6437
23.88	1.6255	1.6360	1.6442
35.35	1.6268	1.6366	1.6444
46.02	1.6285	1.6369	1.6455
54.30	1.6303	1.6371	1.6468
61.00	1.6310	1.6369	1.6471
74.05	1.6330	1.6368	1.6493
84.50	1.6346	1.6367	1.6507
94.58	1.6365 =	1.6365	1.6522
100.00	1.6363	1.6371	1.6528

The refractive indices were first plotted against the percentage by weight of ammonium-magnesium chromate in the crystals. They were found to lie upon three curves. At 93 per cent. by weight (about 95 per cent. by volume) α and β become equal and the two curves cross each other (crystals uniaxial). The indices were then plotted against percentage by volume, which in this case is almost identical with the molecular percentage. The diagram (fig. 16)

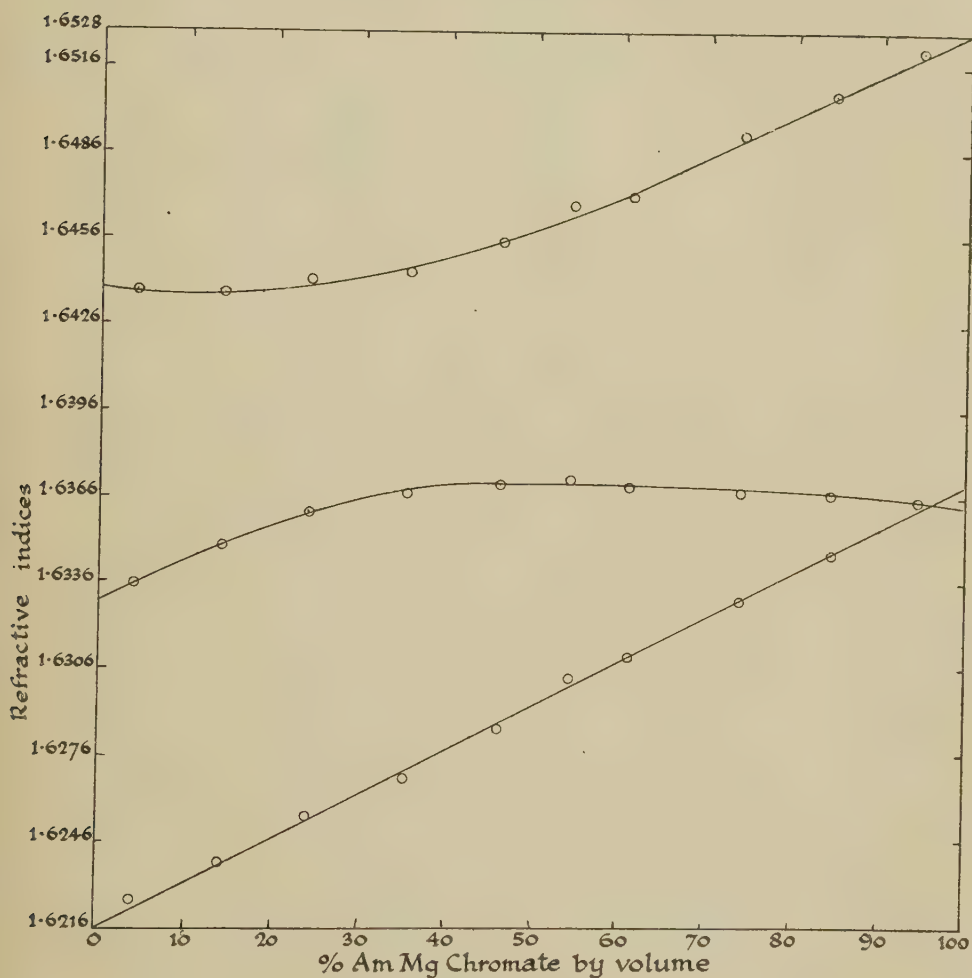


FIG. 16.

shows that the index for vibrations along the symmetry axis (the only direction which in monoclinic crystals is determined by the symmetry of the system and is constant throughout the series) lies on a straight line, whereas the other two lie on curves.

The following table gives the measured indices corresponding to the symmetry axis, compared with the values calculated on the assumption of the linear relation, and shows the agreement to be satisfactory, the differences being of the order of the experimental errors.

Refractive Indices Corresponding to the Symmetry Axis-*b*.

Percentage by volume of ammonium-magnesium chromate.	Measured.	Calculated.	Difference.
4.14	1.6226	1.6222	0.0004
14.17	1.6239	1.6238	0.0001
23.88	1.6255	1.6253	0.0002
35.35	1.6268	1.6270	— 0.0002
46.02	1.6285	1.6285	0.0000
54.30	1.6303	1.6300	0.0003
61.00	1.6310	1.6310	0.0000
74.05	1.6330	1.6331	— 0.0001
84.50	1.6346	1.6347	— 0.0001
94.58	1.6365	1.6362	0.0003

The results may be expressed shortly as follows :—

In mixtures of ammonium and rubidium-magnesium chromates—

(1) The variation of the principal refractive index for vibrations along the symmetry axis is directly proportional to the composition as expressed in volume or molecular percentage, and is represented by a straight line.

(2) The other two principal indices are also continuous functions of the composition, but their variation is represented by curves.

The general result of this investigation in no way conflicts with the work of Lavenir and Dufet on orthorhombic mixtures, but extends it, in so far as it shows that in a monoclinic series of mixed crystals there exists a linear relation between the refractive indices of the mixtures and those of the component salts for that direction for which alone they are comparable throughout the series ; and while failing to distinguish between volume and molecular percentage it shows that the variation of the indices is proportional to one or other of these rather than to percentage by weight.

Further experiments on other pairs of isomorphous salts are in progress.

It gives me great pleasure to offer my sincere thanks to Prof. H. L. Bowman and to Mr. T. V. Barker for valuable suggestions and helpful criticisms during the progress of this research. I have further to thank the Department of Scientific and Industrial Research for their financial assistance towards this work.

Torsional Vibrations in Reciprocating Engine Shafts.

By G. R. GOLDSBROUGH, D.Sc., Armstrong College, Newcastle-on-Tyne.

(Communicated by Prof. T. H. Havelock, F.R.S.—Received May 12, 1925.)

§ 1. *Introduction.*

It is well known that, in the case of reciprocating engines, there are certain critical speeds of running at which the torsional vibrations in the shaft become large in amplitude and introduce an element of danger into the system. Fairly simple methods have been devised for the practical calculation, from the constants of the machinery, of the location of these critical speeds. In these methods, the reciprocating parts of the engine are replaced by an "equivalent mass" which is assumed to contribute to the elastic vibrations of the shaft in exactly the same way as do the actual, rather complicated, system of crank, connecting-rod, piston and piston-rod.* It is the main purpose of this paper to examine the correctness of this equivalence.

In two particular cases examined by the author, the automatic records of the shaft vibrations at about a critical speed showed a large amplitude at the expected point, but the period of the vibration was twice that anticipated. This anomaly is examined on p. 116 and the conditions of its existence exhibited.

The results obtained in this paper are applicable only to relatively low-speed engines. The analysis would require sensible modification to cover speeds amounting to several thousands of revolutions per minute.

§ 2. *Formation of the Equations.*

Consider a dynamical system composed of a crank, a connecting-rod, and a piston. Let the axis of the crank be through O perpendicular to the plane of the paper (fig. 1). Let r be the radius of the crank OB, and l the length of the connecting-rod BA. The piston and piston-rod PA oscillate along OA as OB rotates. Further, let

m_1 be the mass of the piston and piston rod ;

m_2 be the mass of the connecting rod ;

l' be the length GA, where G is the centre of mass of the connecting rod ;

k be the radius of gyration of l about an axis through G parallel to the axis of rotation, and

I be the moment of inertia of the crank about its axis of rotation.

* See, e.g. 'Proc. Inst. Civil Eng.' vol. 162, p. 371.



Then if we take an origin in O, put x for the length OA, θ , measured anti-clockwise for angle AOB, and ϕ for angle BAO, the kinetic energy of such a system is

$$T = \frac{1}{2} [m_1 \dot{x}^2 + m_2 (k^2 + l'^2) \dot{\phi}^2 + m_2 \dot{x}^2 + 2m_2 \dot{x} l' \sin \phi \cdot \dot{\phi} + I \dot{\theta}^2].$$

From the simple relations

$$x = l \cos \phi + r \cos \theta,$$

$$r \sin \theta = l \sin \phi,$$

we can express T in terms of θ and $\dot{\theta}$ alone. It is convenient to expand the formula in powers of μ , which equals r/l . Since r/l is usually about $\frac{1}{4}$ we find a series which converges fairly rapidly. Retaining the terms only as far as μ^2 , we have

$$\begin{aligned} T = & \frac{1}{2} (m_1 + m_2) r^2 \dot{\theta}^2 \left[\frac{1}{2} - \frac{1}{2} \cos 2\theta + \frac{1}{2} \mu (\cos \theta - \cos 3\theta) \right. \\ & \left. + \frac{1}{8} \mu^2 (1 - \cos 2\theta) \dots \right] \\ & + \frac{1}{4} \mu^2 m_2 \dot{\theta}^2 [(1 + \cos 2\theta) (k^2 + l'^2) - r l' (\cos \theta - \cos 3\theta) \dots] \\ & + \frac{1}{2} I \dot{\theta}^2. \end{aligned} \quad (1)$$

It is worth noting that the radius of gyration of the connecting-rod and the position of its centre of mass only appear in terms factored by μ^2 . So that, to the order used, approximate values of these quantities will suffice.

Next consider the thrust applied to the piston by the expanding gases in the cylinder. This thrust is periodic and can be expressed in the form of a Fourier series. But the character of the series will depend upon the type of engine studied. In order to fix ideas we shall consider here only a six-cylinder four-stroke cycle, single-acting Diesel engine. The results obtained can easily be extended to other cases by simple modification of the constants involved. In such an engine the thrust on the piston may be expressed in the form

$$\Sigma a_n \sin n\theta/2 + \Sigma b_n \cos n\theta/2.$$

The period of this series is 4π , corresponding to the two revolutions of the shaft in which the cycle of operations is completed.

The work done in a small displacement δx of the piston is

$$- \delta x \{ \Sigma a_n \sin n\theta/2 + \Sigma b_n \cos n\theta/2 \}.$$

But

$$\delta x = -r (\sin \theta + \frac{1}{2} \mu \sin 2\theta \dots) \delta \theta,$$

the next higher term having the factor μ^3 .

Hence the work done in the small displacement is

$$\begin{aligned} \frac{r}{2} \delta \theta \Sigma [& a_n \{ \cos (n-2) \theta/2 - \cos (n+2) \theta/2 \} \\ & + b_n \{ \sin (n+2) \theta/2 + \sin (n-2) \theta/2 \} \\ & + \frac{1}{2} \mu a_n \{ \cos (n-4) \theta/2 - \cos (n+4) \theta/2 \} \\ & + \frac{1}{2} \mu b_n \{ \sin (n+4) \theta/2 + \sin (n-4) \theta/2 \}]. \end{aligned} \quad (2)$$

If now, we put H_{m-1} and H_m as the torsional couples on either side of the m th crank, we may write the equation of motion of the m th system as :—

$$\begin{aligned} \frac{d}{dt} \frac{\partial T}{\partial \dot{\theta}} - \frac{\partial T}{\partial \theta} = & + r/2 \Sigma [a_n \{ \cos (n-2) \theta/2 - \cos (n+2) \theta/2 \} \\ & + b_n \{ \sin (n+2) \theta/2 + \sin (n-2) \theta/2 \} \\ & + \frac{1}{2} \mu a_n \{ \cos (n-4) \theta/2 - \cos (n+4) \theta/2 \} \\ & + \frac{1}{2} \mu b_n \{ \sin (n+4) \theta/2 + \sin (n-4) \theta/2 \}] \\ & + H_{m-1} - H_m. \end{aligned} \quad (3)$$

Consider now the arrangement of the separate systems along the shaft. First there are the six cranks of the six engine systems and the flywheel separated by short portions of shafting. Then there will be a longer length of shafting connecting with another rotating mass—a propeller in a marine engine or an armature in the case of a dynamo driven by an engine, or perhaps only the rotor of a dynamometer; and this mass operates against a resistance, in overcoming which the energy of the engine is consumed.

We shall assume that this latter resisting couple is uniform and of magnitude H , and that the terminating mass has a moment of inertia about the axis of rotation of magnitude I_p . We shall also take the moment of inertia of the flywheel to be I_f .

All the parts of the mechanism are elastic. We shall, however, in order to reduce the work and secure a first approximation, assume that only the longer part of the shaft is flexible and that all the rest of the material is perfectly rigid. For the purposes of torsional vibrations, it is probable that the portions of the shaft between the various cranks must be considered as elastic. These portions are, however, usually short and stout, and, compared with the longer part of the shaft, may with sufficient accuracy for a first approximation be considered rigid. It is intended to examine this matter in detail in a later paper. We are now considering an engine and flywheel, rigidly connected, operating an elastic shaft with a load at the other end.

Let d be the diameter of this shaft, supposed uniform, L its length, and

μ' the modulus of rigidity of the material of the shaft; then, if we neglect the mass of the shaft itself (this is usually quite small compared with the other masses), the torsional couple producing a difference in angular position of the two ends amounting to ω is $K\omega$, where $K = \frac{1}{32} \pi \mu' d^4 / L$.

The six cranks belonging to the separate cylinders are usually placed at 120° difference in phase. As the crankshaft is assumed rigid, for our purpose it does not matter what the order of the cranks is. We can take it that at any instant the positions of the cranks will be

$$\theta, \theta + 120^\circ, \theta + 240^\circ, \theta + 360^\circ, \theta + 480^\circ, \theta + 600^\circ.$$

Equation (3) will give the expressions for each system in turn if we replace θ by $\theta + 120^\circ, \dots$. On making these substitutions in (3) and adding up the six equations, we find that all the terms disappear, except the constant terms and those which involve circular functions of multiples of 3θ . In particular,

$$T = \frac{1}{2} \dot{\theta}^2 [3(m_1 + m_2)r^2(1 - \mu \cos 3\theta) + 3m_2\mu^2(k^2 + l'^2 + r'l' \cos 3\theta) + 6I].$$

The right-hand side of (3) gives

$$\begin{aligned} & (r/2) [6a_2 + 3\mu a_4] \\ & + 3r [\cos 3\theta \{a_8 - a_4 + \frac{1}{2}\mu(a_{10} - a_2)\} \\ & + \sin 3\theta \{b_4 - b_8 + \frac{1}{2}\mu(b_2 - b_{10})\} \\ & + \cos 6\theta \{-a_{10} - \frac{1}{2}\mu a_8\} \\ & + \sin 6\theta \{b_{10} + \frac{1}{2}\mu b_8\} + \dots] - H_6, \end{aligned}$$

since $H_0 = 0$.

The equation for the flywheel is

$$I_f \ddot{\theta} = H_6 - H',$$

where H' is the couple transmitted to the main shaft. On substituting these values in equations (3) and eliminating H_6 , we find,

$$\begin{aligned} & \ddot{\theta} [3r^2(m_1 + m_2) + 3m_2\mu^2(k^2 + l'^2) + 6I + I_f \\ & - \{3\mu r^2(m_1 + m_2) - 3m_2\mu^2 r l'\} \cos 3\theta] \\ & + \frac{3}{2} \dot{\theta}^2 [\mu(m_1 + m_2)r^2 - \mu^2 m_2 r l'] \sin 3\theta \\ & = r(3a_2 + 3/2\mu a_4) \\ & + 3r [\cos 3\theta \{a_8 - a_4 + \frac{1}{2}\mu(a_{10} - a_2)\} \\ & + \sin 3\theta \{b_4 - b_8 + \frac{1}{2}\mu(b_2 - b_{10})\} \\ & + \cos 6\theta \{-a_{10} - \frac{1}{2}\mu a_8\} \\ & + \sin 6\theta \{b_{10} + \frac{1}{2}\mu b_8\} + \dots] - H'. \end{aligned} \tag{4}$$

θ is the angular displacement of the flexible shaft at the flywheel end. This will produce a torsional couple which will be transmitted to the opposite end. Let ψ be the angular displacement at the latter. Then the couple transmitted is

$$K (\theta - \psi).$$

This couple produces an acceleration $\ddot{\psi}$ in the mass of moment of inertia I_p and also overcomes the resisting couple there, viz., H .

Hence we have

$$\text{and } \left. \begin{aligned} I_p \ddot{\psi} &= K (\theta - \psi) - H \\ H' &= K (\theta - \psi) \end{aligned} \right\}. \quad (5)$$

These give the equations

$$\left. \begin{aligned} &\ddot{\theta} [3r^2 (m_1 + m_2) + 3m_2 \mu^2 (k^2 + l'^2) + 6I + I_f \\ &\quad - \{3\mu r^2 (m_1 + m_2) - 3m_2 \mu^2 r l'\} \cos 3\theta] \\ &\quad + \frac{3}{2} \dot{\theta}^2 [\mu (m_1 + m_2) r^2 - \mu^2 m_2 r l'] \sin 3\theta \\ &= r (3a_2 + \frac{3}{2} \mu a_4) + 3r [\cos 3\theta \{a_8 - a_4 + \frac{1}{2} \mu (a_{10} - a_2)\} \\ &\quad + \sin 3\theta \{b_4 - b_8 + \frac{1}{2} \mu (b_2 - b_{10})\} \\ &\quad + \cos 6\theta \{-a_{10} - \frac{1}{2} \mu a_8\} \\ &\quad + \sin 6\theta \{b_{10} + \frac{1}{2} \mu b_8\} \dots] \\ &\quad - K (\theta - \psi), \end{aligned} \right\}. \quad (6)$$

$$I_p \ddot{\psi} = K (\theta - \psi) - H.$$

These equations, within the small restrictions already stated, completely express the motion of the engine and shaft.

Inspection shows at once that these equations have not even a particular solution representing uniform rotation, owing to the presence of the trigonometric terms. It is further clear that, since the mean applied couple must be equal to the mean resistance,

$$H = r (3a_2 + \frac{3}{2} \mu a_4),$$

and $K (\theta - \psi)$ must contain a constant part equal to H . This constant part in the difference of θ and ψ represents the mean twist of the shaft when under torsional stress.

It is known from experience that uniform angular velocity is an approximation to the motion defined by the equations (6). We shall therefore assume that the motion can be represented by fluctuations about steady motion and seek to determine the nature of these fluctuations.

§ 3. *Solution of the Equations.*

In the left-hand member of the first of equations (6) the trigonometric terms represent the effects of the inertia of the reciprocating parts. The usual plan of replacing these by a single equivalent mass leads only to the term

$$\ddot{\theta} [3r^2 (m_1 + m_2) + 3m_2\mu^2 (k^2 + l'^2) + 6I + I_f].$$

The term in the squared brackets is the "equivalent mass" of the engine system, and this is the only term generally used. But it is evident that the term factored by $\ddot{\theta}^2$ is too important to be rejected without scrutiny. Especially in the cases of higher velocities this term must increase in importance.

We shall assume the mean angular velocity to be ω , and, to find the oscillations about this mean value, we shall assume

$$\left. \begin{aligned} \theta &= \omega t + \xi, \\ \psi &= \omega t - \bar{\psi} + \eta \end{aligned} \right\}. \quad (7)$$

The substitution of these values in the left-hand members of (6) takes an approximately full account of the inertia of the system. In the trigonometric terms of the right-hand member we shall omit the variation ξ . Its inclusion would represent the effects of the oscillations in modifying the compression of the gases in the cylinder, and these we omit in order to keep the equations of manageable size.

Further to simplify the work, we shall retain only linear terms in ξ and η .

The quantity $\bar{\psi}$ is the mean difference between θ and ψ , and is such that $K\bar{\psi} = H$. Now divide the first of equations (6) through by

$$I' = 3r^2 (m_1 + m_2) + 3m_2\mu^2 (k^2 + l'^2) + 6I + I_f;$$

put

$$\{3\mu r^2 (m_1 + m_2) - 3\mu^2 m_2 l'\} \div I' = \varepsilon;$$

change the independent variable from t to τ , $= 3\omega t$, and indicate differentiation with regard to τ by dashes. Then

$$\left. \begin{aligned} \theta'' (1 - \varepsilon \cos 3\theta) + \frac{3}{2} \theta'^2 \varepsilon \sin 3\theta \\ &= H/9I'\omega^2 + f_1 \cos 3\theta + f_2 \cos 6\theta \\ &\quad + g_1 \sin 3\theta + g_2 \sin 6\theta - K(\theta - \psi)/9I'\omega^2, \\ \psi'' &= K(\theta - \psi)/9I_p\omega^2 - H/9I_p\omega^2 \end{aligned} \right\}. \quad (8)$$

In these equations we have written,

$$\begin{aligned} f_1 &= 3r \{a_8 - a_4 + \tfrac{1}{2}\mu (a_{10} - a_2)\} \div 9\omega^2 I', \\ f_2 &= 3r (-a_{10} - \tfrac{1}{2}\mu a_8) \div 9\omega^2 I', \\ g_1 &= 3r \{b_4 - b_8 + \tfrac{1}{2}\mu (b_2 - b_{10})\} \div 9\omega^2 I', \\ g_2 &= 3r (b_{10} + \tfrac{1}{2}\mu b_8) \div 9\omega^2 I'. \end{aligned}$$

Now substitute (7) in (8) except in the trigonometric terms of the right-hand member, and putting for short

$$\kappa_1 = K/9I'\omega^2, \quad \kappa_2 = K/9I_p\omega^2,$$

we have

$$\begin{aligned} \xi'' (1 - \varepsilon \cos \tau) + \kappa_1 (\xi - \eta) + \varepsilon (\xi' \sin \tau + \tfrac{1}{2}\xi \cos \tau) \\ = -\tfrac{1}{6}\varepsilon \sin \tau + f_1 \cos \tau + f_2 \cos 2\tau + g_1 \sin \tau + g_2 \sin 2\tau, \\ \eta'' + \kappa_2 (\eta - \xi) = 0. \end{aligned}$$

The quantity ε is small compared with unity and we shall treat it as of the first order of small quantities. The quantities f and g are also of the first order of smallness. Hence working to this order only,

$$\left. \begin{aligned} \xi'' + \kappa_1 (\xi - \eta) (1 + \varepsilon \cos \tau) + \varepsilon (\xi' \sin \tau + \tfrac{1}{2}\xi \cos \tau) \\ = -\tfrac{1}{6}\varepsilon \sin \tau + f_1 \cos \tau + f_2 \cos 2\tau + g_1 \sin \tau + g_2 \sin 2\tau, \\ \eta'' + \kappa_2 (\eta - \xi) = 0. \end{aligned} \right\} \quad (9)$$

Or, finally, on eliminating ξ ,

$$\begin{aligned} \eta'''' + (\kappa_1 + \kappa_2) \eta'' - \varepsilon \{ -\kappa_1 \eta'' \cos \tau - (\eta'''' + \kappa_2 \eta') \sin \tau - \tfrac{1}{2} (\eta'' + \kappa_2 \eta) \cos \tau \} \\ = -\tfrac{1}{6}\varepsilon \sin \tau + f_1 \cos \tau + f_2 \cos 2\tau + g_1 \sin \tau + g_2 \sin 2\tau. \quad (10) \end{aligned}$$

If we remove the pressures of the gases on the pistons, that is, in equation (6) put H , and all the a 's and b 's zero, and as a consequence put $\bar{\psi}$ in (7) also zero, equation (10) would still have the same form except that f_1, f_2, g_1 and g_2 would be zero. The term $-\tfrac{1}{6}\varepsilon \sin \tau$ is still outstanding in the right member and introduces something of the nature of a forced oscillation. It arises from the incomplete balance of the reciprocating parts.

Omitting completely the right member of (10), we have a linear homogeneous equation with periodic coefficients. The roots of the characteristic equation are readily found to be $\pm \kappa, 0, 0$, where $\kappa^2 = \kappa_1 + \kappa_2$. We shall proceed to the solution on the supposition that κ is not an integer. Take first the solution in the vicinity of the zero roots. Theory shows that this has the form

$$\begin{aligned} \eta &= e^{\sigma\tau} y, \\ y &= \eta_0 + \varepsilon^{\frac{1}{2}} \eta_1 + \varepsilon \eta_2 + \dots, \\ \sigma &= \varepsilon^{\frac{1}{2}} \sigma_1 + \varepsilon \sigma_2 + \dots; \end{aligned}$$

and y is purely periodic of period 2π .

On substituting in (10) the given value for η , we find

$$\begin{aligned} & y'''' + 4\sigma y''' + 6\sigma^2 y'' + 4\sigma^3 y' + \sigma^4 y \\ & + \kappa^2 (y'' + 2\sigma y' + \sigma^2 y) \\ & + \varepsilon \{ \kappa_1 \cos \tau (y'' + 2\sigma y' + \sigma^2 y) + \sin \tau (y''' + 3\sigma y'' + 3\sigma^2 y' + \sigma^3 y \\ & + \kappa_2 y' + \kappa_2 \sigma y) + \tfrac{1}{2} \cos \tau (y'' + 2\sigma y' + \sigma^2 y + \kappa_2 y) \} = 0. \end{aligned}$$

Now introduce the values for y and σ , and we have for the terms independent of ε ,

$$\eta_0'''' + \kappa^2 \eta_0'' = 0.$$

The solution of this of period 2π , is

$$\eta_0 = \text{a constant} = c_0.$$

To make the solution quite complete we require certain initial conditions. We shall assume that when $\tau = 0$, $\eta = c_0$. It follows that at $\tau = 0$, $\eta_1 = \eta_2 = \dots = 0$.

The terms in $\varepsilon^{\frac{1}{2}}$ give

$$\eta_1'''' + 4\sigma_1 \eta_0''' + \kappa^2 (\eta_1'' + 2\sigma_1 \eta_0') = 0.$$

This equation leaves σ_1 indeterminate and requires

$$\eta_1 = a_1 \cos \kappa \tau + b_1 \sin \kappa \tau + c_1.$$

The conditions to be fulfilled show that

$$a_1 = b_1 = c_1 = 0.$$

The terms in ε give

$$\begin{aligned} \eta_2'''' + 4\sigma_2 \eta_0''' + 4\sigma_1 \eta_1''' + 6\sigma_1^2 \eta_0'' + \kappa^2 (\eta_2'' + 2\sigma_2 \eta_0' + 2\sigma_1 \eta_1' + \sigma_1^2 \eta_0) \\ = -\tfrac{1}{2} \kappa_2 c_0 \cos \tau. \end{aligned}$$

Since the right-hand side has no constant term, therefore $\sigma_1 = 0$. From this

$$\eta_2 = \frac{-\tfrac{1}{2} \kappa_2 c_0 \cos \tau}{1 - \kappa^2} + a_2 \cos \kappa \tau + b_2 \sin \kappa \tau + c_2.$$

From the conditions to be fulfilled,

$$a_2 = b_2 = 0, \quad \text{and} \quad c_2 = \frac{\tfrac{1}{2} \kappa_2 c_0}{1 - \kappa^2}.$$

From the terms in $\varepsilon^{3/2}$ we have

$$\eta_3'''' + \kappa^2 \eta_3'' = 0,$$

as the other terms cut out. Hence $\eta_3 = 0$ as before

From the terms in ϵ^2 ,

$$\begin{aligned} \eta_4'''' + 4\sigma_2\eta_2''' + \kappa^2(\eta_4'' + 2\sigma_2\eta_2' + \sigma_2^2\eta_0) \\ = -\frac{c_0}{1-\kappa^2} \left[+\frac{1}{4}\kappa_1\kappa_2 - \frac{1}{8}\kappa_2 + \frac{1}{8}\kappa_2^2 + \cos 2\tau \left(\frac{1}{4}\kappa_1\kappa_2 + \frac{3}{8}\kappa_2 - \frac{3}{8}\kappa_2^2 \right) \right. \\ \left. + \frac{1}{4}\kappa_2^2 \cos \tau \right]. \end{aligned}$$

To avoid the explicit appearance of τ we must have

$$\kappa^2\sigma_2^2 = -\frac{\frac{1}{8}\kappa_2}{1-\kappa^2} (2\kappa_1 - 1 + \kappa_2), \quad (11)$$

and then

$$\eta_4 = c_4 - \frac{c_0 \left(\frac{1}{4}\kappa_1\kappa_2 + \frac{3}{8}\kappa_2 - \frac{3}{8}\kappa_2^2 \right) \cos 2\tau}{4(1-\kappa^2)(4-\kappa^2)} - \frac{\frac{1}{4}c_0\kappa_2^2}{(1-\kappa^2)^2} \cos \tau. \quad (12)$$

It is not necessary to proceed to higher terms of this series.

We pass next to the solutions associated with the roots $\pm \iota\kappa$ of the characteristic equation. In this case the solution has the form

$$\begin{aligned} \eta &= e^{\sigma\tau}y, \\ y &= \eta_0 + \epsilon\eta_1 + \epsilon^2\eta_2 + \dots, \\ \sigma &= \iota\kappa + \epsilon\sigma_1 + \epsilon^2\sigma_2 + \dots; \end{aligned}$$

and y , as before, has the period 2π .

On substituting, we have, for the terms independent of ϵ ,

$$\eta_0'''' + 4\iota\kappa\eta_0''' - 5\kappa^2\eta_0'' - 2\iota\kappa^3\eta_0' = 0.$$

The only solution of this which is periodic, of period 2π , is

$$\eta_0 = \text{a constant} = c_0.$$

The terms in ϵ give

$$\eta_1'''' + 4\iota\kappa\eta_1''' - 5\kappa^2\eta_1'' - 2\iota\kappa^3\eta_1' - 2\iota\kappa^3\sigma_1\eta_0 = -\frac{1}{2}\kappa_2\eta_0 \cos \tau.$$

Therefore $\sigma_1 = 0$, and

$$\eta_1 = c_1 - \frac{\frac{1}{2}\kappa_2\eta_0 \cos \tau}{(1-\kappa^2)^2(1-2\kappa)^2} (1+5\kappa^2) - \frac{\frac{1}{2}\kappa_2(4\iota\kappa-2\iota\kappa^3)\eta_0 \sin \tau}{(1-\kappa^2)^2(1-2\kappa)^2}.$$

On applying the condition that $\eta_1 = 0$, when $\tau = 0$, we have finally,

$$\eta_1 = \frac{\frac{1}{2}c_0\kappa_2}{(1-\kappa^2)^2(1-2\kappa)^2} \{1+5\kappa^2 - (1+5\kappa^2) \cos \tau - (4\iota\kappa-2\iota\kappa^3) \sin \tau\}. \quad (13)$$

The terms in ϵ^2 give the equation

$$\begin{aligned} \eta_2'''' + 4\iota\kappa\eta_2''' - 5\kappa^2\eta_2'' - 2\iota\kappa^3\eta_2' - 2\iota\kappa^3\sigma_2\eta_0 \\ = \frac{\frac{1}{4}c_0\kappa_2(1+5\kappa^2)}{(1-\kappa^2)^2(1-2\kappa)^2} \left(\kappa_1 + \frac{\kappa_2}{2} - \frac{1}{2} \right) + \text{periodic terms.} \end{aligned}$$

Hence

$$-2\kappa^3\sigma_2 = \frac{\frac{1}{4}\kappa_2(1+5\kappa^2)(\kappa_1+\frac{1}{2}\kappa_2-\frac{1}{2})}{(1-\kappa^2)^2(1-2\kappa)^2}. \quad (14)$$

It is unnecessary to carry the calculation of these quantities any further.

By changing the sign of κ in (13) and (14), we can obtain the solution corresponding to the other root, $-\kappa$, of the characteristic equation.

Collecting up the results we see that the integral sought has the form

$$\eta = c_1 e^{\sigma_{(1)}\tau} y_1 + c_2 e^{\sigma_{(2)}\tau} y_2 + c_3 e^{\sigma_{(3)}\tau} y_3 + c_4 e^{\sigma_{(4)}\tau} y_4,$$

where $\sigma_{(1)}$ and $\sigma_{(2)}$ are given by (12) and $\sigma_{(3)}$ and $\sigma_{(4)}$ can be inferred from (14). Inspection shows that in general the characteristic exponents σ are distinct and none of them are congruent to zero, mod. $\sqrt{-1}$.

To complete the solution of equation (10) we must take account of the right-hand member. Without working out the result in detail we can infer the nature of this particular integral. Since the right-hand member of (10) is purely periodic, with period 2π , and the solutions already found of the equation without this member have their characteristic exponents unequal and none of them congruent to zero, mod. $\sqrt{-1}$, except, it may be, in special cases, it follows that the particular integral sought will also be purely periodic, and will contain no real exponents and no terms involving the time explicitly.

§ 4. *Examination of the Solutions Found.*

It is necessary now to examine the solutions found in the last section in order to determine under what conditions, if any, they are valid, and also to see what types of motion they indicate. We have determined the solution in the form of a power series in the quantity ε . The general theory of linear equations of this type shows that the series will be convergent for all time for value of ε sufficiently small, except at, and in the neighbourhood of, critical points. Though we have determined very few of the terms of the various series, it is clear from inspection of the results (11) to (14) that critical points occur at $\kappa^2 = 1, 4, \dots$; that is, whenever κ is an integer. In these cases the solutions already given will fail; and in the vicinity of these critical points the results will be of doubtful value. We must, therefore, construct fresh solutions valid in the neighbourhood of, and at, these critical points.

Keeping clear of their particular values, we can examine the nature of the motion given by the solutions.

Referring to the characteristic exponents, that determined by (14) will always be imaginary within the region of its validity as also is its conjugate

term. These, therefore, will not give rise to anything exceptional in the motion. The exponents determined by (11), however, seem to be almost entirely real. Since $\kappa_1 + \kappa_2 = \kappa^2$, we may write this expression

$$\kappa^2 \sigma_2^2 = -\frac{1}{8} \kappa_2 \left(-1 + \frac{\kappa_1}{1 - \kappa^2} \right).$$

So that except for values of $\kappa_1 > 1 - \kappa^2$, σ_2^2 is a real positive quantity. This is the more emphasised in that κ_1 is usually small in comparison with κ_2 . It would, then, appear as though the vibrations given by this expression would increase slowly in amplitude, for a large range of values in the constants, in the entire absence of friction.

The vibrations included in the particular integral are everywhere finite in amplitude, except in the vicinity of the critical points mentioned.

§ 5. *Solution of the Equations in Critical Cases.*

I. $\kappa = 1$.—Returning now to equation (10) we shall find the solution valid for the critical case $\kappa = 1$. In order, however, to cover more than the exact critical point, we shall put $\kappa^2 = 1 + \alpha \epsilon^2$, where α is a small variable quantity. The equation then becomes

$$\eta'''' + \eta'' (1 + \alpha \epsilon^2) = -\epsilon \{ \eta'' \cos \tau + (\eta''' + \kappa_2 \eta') \sin \tau + \frac{1}{2} (\eta'' + \kappa_2 \eta) \cos \tau \} \\ + (g_1 - \frac{1}{6} \epsilon) \sin \tau + g_2 \sin 2\tau + f_1 \cos \tau + f_2 \cos 2\tau. \quad (15)$$

We shall take the equation first without the last member, and so study the homogeneous part.

As before,* put

$$\eta = e^{\sigma \tau} y, \\ y = \eta_0 + \epsilon \eta_1 + \epsilon^2 \eta_2 + \dots, \\ \sigma = \epsilon \sigma_1 + \epsilon^2 \sigma_2 + \dots$$

On substituting the terms without ϵ give

$$\eta_0 = a_0 + b_0 \cos \tau + c_0 \sin \tau,$$

where a_0 , b_0 and c_0 are arbitrary constants.

The terms in ϵ give

$$\eta_1'''' + 4\sigma_1 \eta_0''' + \eta_1'' + 2\sigma_1 \eta_0' = -\Theta(\eta_0),$$

where we have written

$$\Theta(\eta) = \eta'' \cos \tau + (\eta''' + \kappa_2 \eta') \sin \tau + \frac{1}{2} (\eta'' + \kappa_2 \eta) \cos \tau.$$

* The tacit assumption that y and σ are expansible in simple power series in ϵ can be justified by suitable modifications of the usual existence theorems.

To avoid the constant terms appearing in Θ we must have

$$b_0 = 0.$$

Also, to remove the term in $\cos \tau$,

$$2\sigma_1 c_0 = \kappa_2 a_0; \quad (16)$$

and, finally,

$$\eta_1 = a_1 + b_1 \cos \tau + c_1 \sin \tau + \frac{1}{48} (5 - 3\kappa_2) c_0 \sin 2\tau. \quad (17)$$

Up to this stage, the quantities σ_1 and one of the two quantities a_0, c_0 remain undetermined. The terms of the original equation factored by ε^2 give

$$\begin{aligned} \eta_2'''' + 4\sigma_1 \eta_1''' + 4\sigma_2 \eta_0''' + 6\sigma_1^2 \eta_0'' + \eta_2'' + 2\sigma_1 \eta_1' + 2\sigma_2 \eta_0' \\ + \sigma_1^2 \eta_0 + \alpha \eta_0'' = -\Theta(\eta_1). \end{aligned} \quad (18)$$

On picking out from $\Theta(\eta_1)$ the constant terms and those involving $\cos \tau$ and $\sin \tau$, we have the equations

$$\sigma_1^2 a_0 = b_1/4 (5 - 3\kappa_2), \quad (19)$$

$$2\sigma_1 b_1 - \alpha c_0 - 5\sigma_1^2 c_0 = \frac{1}{192} (5 - 3\kappa_2) (-4 + 3\kappa_2) c_0, \quad (20)$$

$$-2\sigma_1 c_1 - 2\sigma_2 c_0 = -\frac{1}{2} \kappa_2 a_1. \quad (21)$$

On eliminating a_0, c_0 and b_1 from the equations (16), (19) and (20) we arrive at the equation for σ_1 , which is

$$\begin{aligned} 32\sigma_1^4 - 5\kappa_2 (5 - 3\kappa_2) \sigma_1^2 + \kappa_2/192 (5 - 3\kappa_2)^2 (4 - 3\kappa_2) \\ - \alpha \kappa_2 (5 - 3\kappa_2) = 0. \end{aligned} \quad (22)$$

When σ_1 has been determined from this equation, (20) determines c_0 in terms of a_0 , which we may regard as arbitrary, and (19) determines b_1 in terms of a_0 . The relation (21) gives one equation for determining σ_2 corresponding to (16) for σ_1 . For the complete evaluation of σ_2 and c_1 , we must proceed to the equation formed by the terms factored by ε^3 .

So far as the work has been carried, the exponent σ is known up to the first power of ε . This is sufficient to give a clear idea of the motion, and the approximations are carried no further.

II. $\kappa = 2$.—We proceed next to the case where the quantity κ approaches the next critical value and, in equation (10) we put $\kappa^2 = 4 + \alpha\varepsilon^2$. The solution follows the same lines as before, and it is only necessary to write down the final results.

The values of the constants fall into two separate groups :—

$$(a) \quad \sigma_1^2 = \frac{1}{96} \kappa_2 (1 + \kappa_2), \quad (23)$$

a_0 is arbitrary,

$$b_0 = c_0 = 0,$$

$$b_1 = 0,$$

$$c_1 = -\frac{a_0 \kappa_2 (5 - 3\kappa_2)}{384 \sigma_1},$$

$$a_1 = -\frac{1}{6} \kappa_2 a_0,$$

$$\eta_1 = a_1 + c_1 \sin 2\tau + \frac{1}{6} a_0 \kappa_2 \cos \tau.$$

$$(b) \quad \sigma_1 = 0,$$

$$256\sigma_2^2 + \{16\alpha + \frac{1}{7\frac{1}{2}0} (110\kappa_2^2 - 130\kappa_2 - 456)\} \\ \{16\alpha + \frac{1}{7\frac{1}{2}0} (-25\kappa_2^2 + 275\kappa_2 - 756)\} = 0, \quad (24)$$

$$b_0 = -\frac{2\kappa_2}{4 - 3\kappa_2} a_0,$$

$$c_0 = \frac{1}{16\sigma_2} \{-16\alpha + \frac{1}{7\frac{1}{2}0} (-25\kappa_2^2 + 275\kappa_2 - 756)\} b_0.$$

Equations (23) and (24) show four values of the exponent σ , thus completing the necessary number. In a similar fashion we could determine the solutions in the vicinity of $\kappa = 3, 4, \dots$.

§ 6. *Examination of the Solutions Found in § 5.*

Before proceeding to find the particular integrals of the equation (10) under different conditions, it is of service to examine the partial solutions already found. The character of the solution is fixed by the nature of the exponent σ , as the co-factor of the exponent is purely periodic in each case.

(1) *Case when $\kappa = 1$.*—The index σ is in the nature of a series, $\sigma = \varepsilon\sigma_1 + \varepsilon^2\sigma_2 \dots$. As ε is known to be a very small quantity, we have merely determined the first term. The four values of σ_1 are given by equation (22), which we repeat :—

$$32\sigma_1^4 - 5\kappa_2 (5 - 3\kappa_2) \sigma_1^2 + \frac{\kappa_2}{192} (5 - 3\kappa_2)^2 (4 - 3\kappa_2) \\ - \alpha \kappa_2 (5 - 3\kappa_2) = 0. \quad (25)$$

In this equation κ_2 is a constant, depending upon the masses of the reciprocating machine and the other constants of the motion. The quantity α is a variable parameter, introduced to give an idea of the character of the motion near to the critical point $\kappa = 1$.

If the equation (25) has as a solution for σ_1 a positive real value, then the motion tends to depart largely from uniform angular velocity, though it is clear, of course, that with lapse of time the original equations, framed on the assumption of small values of ξ and η , break down. On the other hand, purely imaginary values of σ_1 mean that the motion consists of small variations about uniform angular velocity. We therefore proceed to examine the nature of the roots of this bi-quadratic equation.

Since $\kappa_1 + \kappa_2 = 1 + \varepsilon^2\alpha$, and the last term is small, $\kappa_2 < 1$. Hence the factors $(5 - 3\kappa_2)$ and $(4 - 3\kappa_2)$ are positive.

Now consider the case when $\alpha = 0$. It is easily found that if $\kappa_2 > \text{about } 0.1$, the values of σ_1^2 are both real and positive. Even if this condition regarding κ_2 is not fulfilled, the real part of the value of σ_1^2 will always exist and will be positive. Hence in both cases we shall have one pair of values of σ_1 with their real parts positive. The introduction of a positive value for α makes the values of σ_1^2 more certainly real, one value of σ_1^2 becoming greater and the other less. Ultimately, when

$$\alpha = \frac{(5 - 3\kappa_2)(4 - 3\kappa_2)}{192}$$

we have one pair of values of σ_1 zero. This is an important point.

When a negative value of α is taken, the values of σ_1^2 tend to be more certainly complex; but the real parts remain positive and the results are as before. There is clearly no value of α that would make the values of σ_1 purely imaginary. Hence it can be said definitely that at every point in the vicinity of $\kappa = 1$ the vibrations increase in amplitude with the time.

(ii) *Case when $\kappa = 2$.*—The four values of the exponent are given by (23) and (24). The first is always real and positive, the second real and negative. Both are independent of α , and the former indicates, in the vicinity of $\kappa = 2$, vibrations of increasing amplitude. The third and fourth indices begin with $\varepsilon^2\sigma_2$, and hence are extremely small. In the expression (29) the quantity $(-25\kappa_2^2 + 275\kappa_2 - 756)$ is negative for $0 < \kappa_2 < 4$; the quantity $(110\kappa_2^2 - 130\kappa_2 - 456)$ is negative for values of κ_2 between 0 and about 2.7, but for higher values of κ_2 is positive. Hence, when $\alpha = 0$ and $\kappa_2 < 2.7$, σ^2 is real and negative. The motion then shows no tendency to exaggerated amplitudes of vibration. If, on the other hand, $\kappa_2 > 2.7$, as is the case in many types of engine, σ^2 is real and positive and the motion will exhibit vibrations of increasing amplitude at the critical point.

A pair of zero values of σ_2 occurs at

and
$$\left. \begin{aligned} \alpha &= \frac{1}{11520} (456 + 130\kappa_2 - 110 \kappa_2^2) \\ \alpha &= \frac{1}{11520} (756 - 275\kappa_2 + 25\kappa_2^2) \end{aligned} \right\}. \quad (26)$$

These indicate two points very close together, which may or may not include the point $\kappa = 2$ between them, though it must always be near them. When α has a value intermediate to these two values, σ_2^2 is real and positive and the vibrations have increasing amplitudes. Outside this range the motion shows no such increase in amplitudes.

§7. *The Nature of the particular Integrals in the Critical Cases.*

Having found the solutions of equation (10) without the right-hand member, we now proceed to discuss the nature of the particular integrals when that member is included. We can infer a good deal about these integrals from the general theory of such equations already quoted. The right-hand member is purely periodic of period 2π . If, then, the characteristic exponents already found are all unequal and none of them congruent to zero mod. $\sqrt{-1}$, then it is known that the particular integrals will also be purely periodic. But if either of these conditions is unfulfilled, the particular integrals will involve the time explicitly. From the nature of the case, none of the characteristic exponents can be equal to an imaginary integer. But we do have certain pairs of exponents equal to zero. When $\kappa^2 = 1 + \varepsilon^2\alpha$, this occurs, as already shown, at

$$\alpha = \frac{(5 - 3\kappa_2)(4 - 3\kappa_2)}{192}.$$

Owing to the smallness of ε , this occurs very close to the point $\kappa = 1$. But it is important to notice that this occurs independently of the type of term in the right-hand member. All that is requisite is that the term should be periodic.

Again, in the vicinity of $\kappa = 2$, the exponents given by (23) lead to no terms in the particular integral other than periodic terms.

The exponents given by (24) produce terms involving the time explicitly in the particular integrals at the points indicated by (26). In practice these points are close together and very close to the point $\kappa = 2$.

The right-hand member of equation (10) has the value

$$-\frac{1}{6} \varepsilon \sin \tau + f_1 \cos \tau + f_2 \cos 2\tau + g_1 \sin \tau + g_2 \sin 2\tau.$$

$$\left. \begin{aligned} (1^2 - \kappa^2) B_1 + q_2 B_2 &= g_1 - \frac{1}{6}\varepsilon, \\ p_1 B_1 + 2^2 (2^2 - \kappa^2) B_3 &= g_2, \\ p_2 B_2 + 3^2 (3^2 - \kappa^2) B_3 + q_4 B_4 &= 0, \\ \dots &\dots \\ p_{n-1} B_{n-1} + n^2 (n^2 - \kappa^2) B_n + q_{n+1} B_{n+1} &= 0, \\ \dots &\dots \end{aligned} \right\} \quad (28)$$

The general relation between the coefficients is of a well-known form.* It is readily shown that the sequence of coefficients forms an absolutely convergent series, provided we add the further condition that

$$\lim_{n \rightarrow \infty} \frac{B_{n+1}}{B_n} = 0.$$

In practice, the application of this condition amounts to the replacement of a finite series for the infinite series, the finite series stopping at some term B_n such that B_{n+1}/B_n would be less than a certain quantity which is regarded as the lower limit of magnitudes to be considered.

Working, then, with the finite series, and writing

$$\Delta = \begin{vmatrix} 1^2 - \kappa^2, & q_2, & 0, & 0, & 0 \\ p_1, & 2^2(2^2 - \kappa^2), & q_3, & 0, & 0 \\ 0, & p_2, & 3^2(3^2 - \kappa^2), & q_4, & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \dots, & \dots, & p_{n-2}, & (n-1)^2\{(n-1)^2 - \kappa^2\}, & q_n \\ \dots, & \dots, & 0, & p_{n-1}, & n^2(n^2 - \kappa^2) \end{vmatrix},$$

and

Δ_r the same determinant in which the r th column has its first and second members replaced by $g_1 - \frac{1}{6}\varepsilon$ and g_2 , respectively, the remaining members of that column being all zero. Then the solution of the equations (28) is

$$B_r = \Delta_r \div \Delta,$$

for all values of r from 1 to n . And the particular integral of equation (27) is

$$\eta = \Sigma \Delta_r \sin r\tau / \Delta. \tag{29}$$

It is clear from this solution that in those positions where Δ is small the amplitudes of the harmonic terms increase; and when Δ vanishes the solution as it stands fails. But it is readily shown that in the latter case, by the device commonly used for this type of equation, there appears a factor τ explicitly attached to the coefficient of each term.

This corresponds closely with what we found in an entirely different way in the last section. It is to be noticed that as the p 's and q 's all have the factor ε , which is small, the value of Δ is small whenever κ is an integer. But Δ

* Cf. Lamb: 'Hydrodynamics' (Fourth Edition), p. 323; and 'Proc. Lond. Math. Soc.,' Ser. 2, vol. 14, p. 38.

does not rigorously vanish for any integral value of κ . We may put it that the necessary value of κ for that purpose has the form $\kappa^2 = r^2 + \alpha\epsilon^2$, where r is an integer and α is small. In fact, the solution of the equation $\Delta = 0$ should give the same values of α in the vicinity of $r = 1$ and $r = 2$, as we have already found by the other method.

Now let $\Delta^{(r)}$ be the determinant formed by deleting from the determinant Δ the first $(r-1)$ rows and columns. Then

$$\begin{aligned} B_1 &= \{(g_1 - \tfrac{1}{6}\epsilon) \Delta^{(2)} - g_2 q_2 \Delta^{(3)}\} \div \Delta, \\ B_2 &= \{(1^2 - \kappa^2) g_2 \Delta^{(3)} - p_1 (g_1 - \tfrac{1}{6}\epsilon) \Delta^{(3)}\} \div \Delta, \\ &\text{and so on.} \end{aligned}$$

Now, suppose $g_1 = g_2 = 0$. That is, we have in the right-hand member of equation (27) only the term $-\frac{1}{6}\epsilon \sin \tau$, which arises from the inertia of the reciprocating machinery, and no actual external force acting on the system. Suppose, further, that $\kappa = 2$. We shall avoid the complication of $\Delta = 0$ by considering what happens when Δ is small, because $\kappa = 2$. Then

$$\begin{aligned} B_1 &= -\tfrac{1}{6}\epsilon \Delta^{(2)} / \Delta, \\ B_2 &= -\tfrac{1}{6}\epsilon p_1 \Delta^{(3)} / \Delta. \end{aligned}$$

But, as $\kappa = 2$,

$$\Delta^{(2)} = -p_2 q_3 \Delta^{(4)}.$$

Hence

$$B_2 / B_1 = -p_1 \Delta^{(3)} \div p_2 q_3 \Delta^{(4)}.$$

Now the first terms respectively of $\Delta^{(3)}$ and $\Delta^{(4)}$ are independent of ϵ , and that of $\Delta^{(3)}$ is greater (numerically) than that of $\Delta^{(4)}$. So that, for sufficiently small values of ϵ it is evident that B_2 may be made a large multiple of B_1 . In the series for η , in such a case, the term in $\sin 2\tau$ will preponderate, although the motion is excited by a term involving $\sin \tau$ only. We may then expect to find, arising purely from the inertia of the system itself, and apart from any external forces, large vibrations produced in the vicinity of κ equal to an integer.

Again, restoring g_1 and g_2 , it may happen that the constants of the system are such that, in the vicinity of $\kappa = 2$,

$$(1^2 - \kappa^2) g_2 = p_1 (g_1 - \tfrac{1}{6}\epsilon),$$

or, at any rate, the values may be such that the difference of the two members is small compared with

$$\{(g_1 - \tfrac{1}{6}\epsilon) \Delta^{(2)} - g_2 q_2 \Delta^{(3)}\} \div \Delta^{(3)}.$$

In such a case the term of η in $\sin 2\tau$ will be small compared with the term in $\sin \tau$. We should then find that though the vibrations were large they

had the period 2π , and not π , as would be anticipated from the fact that $\kappa = 2$.

This departure from anticipation is exaggerated in calculating the value of ξ . From equation (9)

$$\xi = \eta''/\kappa_2 + \eta.$$

Now in a large number of cases of a certain type κ_2 is large compared with κ_1 . Therefore, since $\kappa_1 + \kappa_2 = \kappa^2 = 4$, approximately, it is clear that κ_2 is also approximately 4. Now, remembering that $\eta = B_1 \sin \tau + B_2 \sin 2\tau + \dots$, and already B_2 is smaller than B_1 , we find

$$\xi = \frac{\kappa_2 - 1}{\kappa_2} B_1 \sin \tau + \frac{\kappa^2 - 4}{\kappa_2} B_2 \sin 2\tau + \dots$$

So that, at this point, the coefficient of $\sin 2\tau$ is still further reduced.

An instrument, therefore, put to register the motion at the engine end of the shaft, would find the vibrations about uniform rotation almost purely of period 2π .*

In the general case, with no particular relations among the terms, the solution given by (34) would show exaggeration of amplitudes in the vicinity of the critical points, but would not show a vibration of simple form; it would be compounded of all the terms of the series, none of which would markedly predominate, but the whole would have period 2π .

The cosine terms of the right-hand member of equation (27), which were omitted, can be handled in exactly the same way as the sine terms and produce similar results. The final value of η is obtained by adding together the two series.

§ 9. *Summary.*

In this paper we have investigated analytically the vibrations about steady motion of an elastic shaft having an engine at one end and a mass operating against a resistance at the other end. The engine is assumed to be of the reciprocating type, and to fix ideas we have taken it to be of the six-cylinder variety of four-stroke, single-acting Diesel engine. To simplify the work we have assumed the engine parts to be rigid. We have taken fully into account the inertia of the reciprocating parts of the engine, but we have omitted entirely any account of the internal resistance to vibration in the flexible shafting and the resistance to vibration which must also occur at the load end of the shaft. The omission is due to our ignorance of the character of these resistances.

* Cf. Rayleigh: 'Phil. Mag.,' vol. 24, 1887, p. 145. A. Stephenson: 'Quarterly Journal of Pure and Applied Mathematics,' vol. 37, p. 353 (1906).

The oscillations about steady rotation are found to be of two types, analogous to free and forced vibrations respectively. The forced vibrations do not arise entirely from the pressure of the expanding gases on the pistons. They are also produced by the incomplete balance of the reciprocating parts. Practically all the phenomena associated with dangerous critical speeds would appear if the fuel were cut off and the engine made to run against no resistance with the requisite speed.

The positions of the critical speeds are approximately those found by the usual methods. Slight differences appear, but in practice they would be probably unimportant.

The vibrations, analogous to free vibrations, appear to be of the form $e^{\sigma t}$ multiplied by periodic terms, where σ is a small constant and t is the time. Throughout the whole range of possible speeds of rotation at least one of the quantities σ appears to have a real part, existing and positive. This would point to the fact that, apart from frictional resistances, the vibrations everywhere tend to increase in amplitude with time. As this is contrary to experience, it is probable that the various kinds of frictional resistance that are possible have the effect of cutting out the real and positive part of σ , or, if not exactly cancelling it, at any rate of leaving the real part negative. This would cause any such vibrations, if at any time excited, to be damped out.

Such frictional resistances would not produce, in the case of vibrations analogous to forced vibrations, any marked change of character. Such change as occurs would be one of degree and not kind. We may then interpret the vibrations of this type as having a direct physical significance.

As in the last case, we find the critical speeds are moved slightly from the values obtained by the approximate theory, but not so much as to be of practical importance. Between the critical speeds the vibrations are small. As already remarked, however, these critical speeds do not arise only from the periodic firing in the cylinders, but also from the incomplete balance of the reciprocating parts. Moreover, the latter is equally effective in point of magnitude in producing large vibrations at certain velocities.

The type of vibration produced is in general very complicated and cannot be definitely said to consist at any speed of a simple vibration of definite period. Two very important facts, however, appear :—

(a) Suppose that the applied force has a term of the form $P \sin 3\omega t$, where ω is the mean angular velocity of the shaft and t is the time. This would correspond to three vibrations in the period of one rotation of the shaft. According to the usual theory, a critical speed would occur whenever the natural frequency

of elastic vibrations of the system was three per revolution of the shaft. It is shown, however, that the same term can produce a critical speed whenever the natural frequency of vibration of the shaft is 3, 6, 9, . . . per revolution of the shaft. This means that the existence of terms such as $\sin 6\omega t$, $\sin 9\omega t$ in the applied force is not essential, and their absence cannot be taken to imply absence of corresponding critical speeds.

(b) Under certain circumstances, depending upon the magnitudes of the parts of the system, in the vicinity of a critical speed corresponding to six vibrations of the shaft per revolution we may find that the curve is not at all like the curve of $\sin 6\omega t$, but is almost exactly $\sin 3\omega t$. The critical speed is right and the vibrations large in amplitude, but the period of the curve of vibrations is twice that anticipated. This explains the phenomenon found in an actual case and automatically registered on a torsiongraph.

High-Frequency Fatigue Tests.

By C. F. JENKIN.

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PART I.

The experiments on high-frequency fatigue in copper, Armco iron, and mild steel described in the following paper were carried out in the Engineering Laboratory, Oxford, for the Fatigue Panel of the Aeronautical Research Committee. The cost of the apparatus was defrayed by a grant from the Engineering Research Board of the Department of Scientific and Industrial Research.

In 1911 Prof. B. Hopkinson* called attention to the importance of ascertaining whether the fatigue limit of metals was dependent on the rate of alternation of stress. He designed and made an electric alternating direct-stress machine, and published the results of tests on mild steel carried out at about 7,000 periods per minute (116 per second), which was more than three times as fast as any tests made up to that time. The results at this speed were compared with those made by Dr. Stanton at the National Physical Laboratory on the same material at 2,000 periods per minute (33 per second).

* 'Roy. Soc. Proc.,' A, vol. 86 (November, 1911).

Prof. Hopkinson considered that the results showed that speed had a marked effect, but he did not consider that his tests were conclusive. In the light of the knowledge gained on fatigue testing since that date neither set of tests can be considered satisfactory. The question is of importance to the users of high-speed machinery. It is also of importance when comparisons are made between tests carried out at different speeds, and, finally, it has a bearing on the causes of fatigue failure. For these reasons it appeared to be desirable to make a more thorough investigation, and, if possible, to extend the tests to very much higher speeds.

None of the methods commonly used for making fatigue tests appeared to be suitable for the speeds contemplated, and the only possible method appeared to be one in which a vibrating spring formed the test piece. The best method of maintaining the vibrations was clearly electrical, and to reduce the power required the resonance method (used by Hopkinson) seemed to be the easiest. The resonance method requires very accurate tuning of the periodicity of the electrical supply; the best method of obtaining a suitable supply appeared to be the use of a thermionic valve and tuned circuit. In all the common forms of fatigue-test machines the maximum stresses occur at the supports or points of application of the load, and to avoid fractures at these points (where the stresses are complex and unknown) the samples have to be turned to a suitable form so as to be stronger at the grips or where the loads are applied. By using a simple beam as a vibrating spring these difficulties disappear, since the maximum stress occurs in the middle and not at the points of support, so that the test piece does not need to be machined but may be of uniform section. Also, the test pieces for all frequencies can be identical except for their length.

No difficulty was experienced in making apparatus to carry out tests on these lines up to 1,000 periods per second. The design is shown in fig. 1. For higher frequencies the difficulties increased, and the design had to be modified. Beyond 2,000 periods per second the method became impossible owing to the shortness of the test pieces. Tests at speeds up to 5,000 periods with a torsion apparatus are described in Part II. Torsional vibrations of large amplitudes at 5,000 periods were successfully produced, but the apparatus was not quite powerful enough to break the specimens, so no fatigue limits could be determined at that speed.

In both the first designs the test piece is a straight rod of round wire, not machined in any way. All the test pieces of each material were cut from single coils of wire, straightened and then heat-treated. The test pieces varied in

length from 19·4 inches (for periodicities of 50 per second) to 2·54 inches (for periodicities of 2,000 per second). The test piece is supported at the nodes

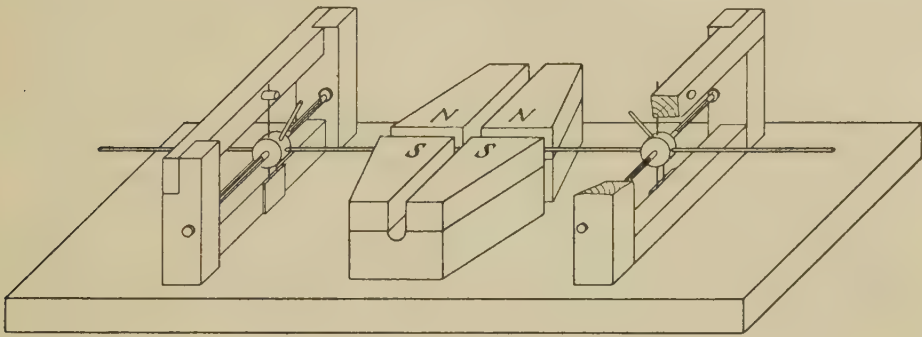


FIG. 1.

in brass trunnions so that it can vibrate freely. The trunnions are attached to the frame by bundles of fine copper wires, which twist backwards and forwards as the test piece vibrates. The trunnions are steadied vertically by three needles, two beneath and one above, the points of the needles being in the axis of the trunnions. The needles can spring towards each other, and thus allow for the very minute changes in length between the trunnions, due to the bending of the specimen. The bundles of wires on each side of the trunnions locate the specimen sideways and also serve as leads to carry the alternating current, which flows through the test piece from one trunnion to the other.

The test piece, supported in this way, is placed between the poles of an electromagnet which produces an approximately uniform horizontal field normal to it. The alternating current flowing along the test piece causes it to vibrate in the magnetic field. By adjusting the frequency of the current so as to be exactly equal to the natural frequency of the test piece the vibrations are maintained with a very small expenditure of power. By regulating the current the amplitude of the vibration can be adjusted to any desired magnitude. The amplitude is measured by means of a microscope. The microscope used for measuring the larger amplitudes* was fitted with an object glass mounted at the end of a thin tube which passes through a slot in the

* The amplitudes (half the total swing) required to break the samples were approximately as follows :—

	50 ~	500 ~	1,000 ~	2,000 ~
Copper	2·8 mm.	0·3 mm.	0·162 mm.	0·08 mm.
Armco	7·27	0·768	0·397	—
Mild steel	7·85	0·808	0·42	—

middle of the pole piece. The microscope is held in a cathetometer, by which it can be raised and lowered; it is focused on the test piece by sliding it in and out of an outer tube. The microscope used for measuring the small amplitudes is fixed in an oblique position, and the measurement is made by means of a cobweb micrometer eyepiece.

The alternating current used to produce the vibrations is obtained from a thermionic valve connected to an oscillating circuit consisting of an inductance and capacity, and the periodicity was adjusted by varying the values of the capacity (a suitable inductance being chosen for each frequency). The electromagnetic forces driving the bar are so small that its shape when bent is almost exactly that assumed by a free bar, the equation to which has been given by Lord Rayleigh,* and therefore the strain in the middle can be calculated from the observed amplitude without appreciable error.

Only three measurements are actually needed to determine the fatigue limits—namely, the amplitude of the vibrations (giving the strain), the frequency, and the duration of the test till fracture occurs. The great difficulty at first was the adjustment and measurement of the frequency. Any modification in an oscillating circuit alters the frequency, and it was found to be impossible to get the apparatus to work, till ammeters, voltmeters, and a wattmeter were inserted in the various circuits so that the effects of each adjustment could be measured. As the total power given by the valve was very small (at first only 10 watts, later 25 watts), very little power was available for these instruments. After a good many trials, satisfactory methods of making all the measurements were found and the apparatus worked well.

Oscillating Circuits.—A great many different arrangements of oscillating circuits were tried. Some were found much more difficult to adjust than others, but there did not seem to be any great differences between the useful powers which could be obtained. The arrangement finally adopted is shown in fig. 2. The induction coil was made with 20 taps, and three 20-point switches were connected to the taps, so that the number of coils in the anode circuit, the condenser circuit, and the power circuit could be varied independently. The reaction coil connected to the grid was provided with six taps; the minimum number of coils which would maintain oscillation was always used in this circuit. A small battery was connected in the grid circuit so that its potential could be adjusted. The induction coil had an iron core made of transformer

* In the 'Theory of Sound.' The mathematical equations for the form assumed by the bar, the position of the nodes, the maximum strain, the deflection at the centre and ends, etc., are collected in the Appendix.

plates. The number of plates used was varied in different tests. Mica condensers were used, subdivided so that any capacity from 2 mfd. down to

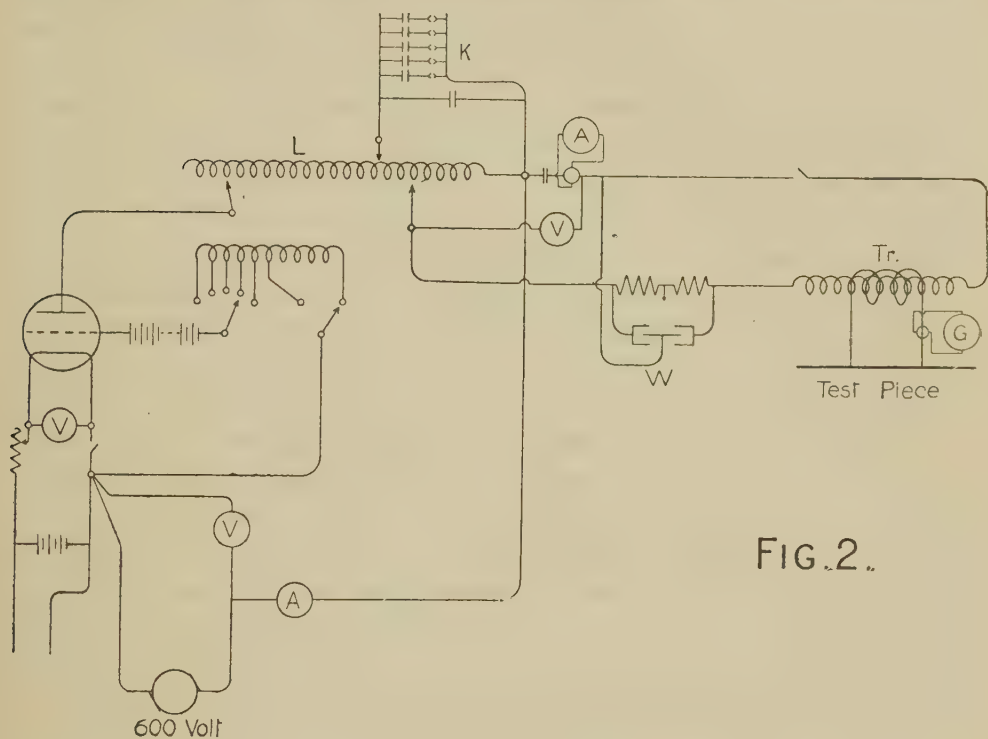


FIG. 2.

FIG. 2.

0.001 mfd. could be plugged into circuit; for fine adjustment a 0.003-mfd. variable-air condenser was used. The anode current was supplied by a 600-volt, $\frac{1}{10}$ -amp., separately excited dynamo, direct-coupled to a $\frac{1}{2}$ -h.p., direct-current motor, running up to 4,000 r.p.m. The commutator and armature slot ripples were eliminated by a choking coil and condenser. A very fine fuse was connected in the circuit, and several times saved accidents. It was made of the finest tungsten wire, given for these experiments by the Director of the General Electric Company's Research Laboratory.

A special transformer was made for transforming the high-tension current given by the valve into the low-tension current required in the test piece, but experience showed that it was no better than a very primitive arrangement made by wrapping two or three turns of heavy flexible cable round a choke coil wound with 2,000 turns. The usual ratio of transformation was 1,000 : 1.

Frequency Measurements.—Acoustical methods with telephones and tuning

forks were first tried, but none of the staff had sufficient musical experience to determine the notes. Various electrical methods of calculating the frequency were then tried, but all were found unreliable, probably owing to the occasional presence of harmonics in the electrical oscillations. Finally, a simple stroboscope was found to answer admirably. It consisted of a small motor which could be run at any speed up to 4,000 r.p.m. ; the spindle was geared to a counter and carried a brass disc on its end. For speeds up to 2,000 periods per sec. the disc had 20 slots cut in it and the end of the vibrating test-piece was looked at through the slots.

Current Measurements.—Small vacuum thermo-junctions such as are commonly used for wireless work answered perfectly. The thermo-junctions were connected to unipivot millivoltmeters which had the series resistances cut out, thus increasing their sensitivity about 50-fold. For measuring the large currents (up to 50 amp.) which were used in the oscillating test piece a shunt was used in series with the current, the potential terminals of the shunt being connected to the smallest available vacuum thermo-junction. The thermo-junction was connected to a d'Arsonval mirror galvanometer of high sensitivity. By keeping the vacuum junction in a lagged box and correcting for a wandering zero, sufficiently accurate readings could be obtained. The shunt consisted of a piece of copper pipe about an inch long and the potential lead was brought out through the pipe so as to eliminate induction. In circuits such as the valve anode circuit which carried both D.C. and A.C., a milliammeter of 1 ohm resistance was connected in series with a vacuum thermo-junction. The values of both A.C. and D.C. components could be calculated from the two readings. In the later experiments a condenser was inserted so as to confine the D.C. to the anode circuit and inductance coil.

Voltage Measurement.—A Kelvin electrostatic voltmeter reading to 80 volts was used. It was connected to a potential divider consisting of a megohm divided in tenths, so that readings up to 800 volts could be made with a maximum expenditure of $\frac{2}{3}$ of a watt. The voltages only occasionally exceeded 300 volts, for which pressure the power absorbed is only 0.1 watt.

Power Measurement.—An electrostatic dynamometer method was used, with a Dolezalek instrument, which absorbed 0.29 watts with the maximum current used. All these instruments were calibrated with direct current.

Voltage Regulations.—One of the fundamental difficulties in making tests on free vibrations is that the periodicity of the power supply must be kept within extremely narrow limits. One of the advantages of using valves for supplying power is that the periodicity of the oscillating current is only slightly

affected by small variations in the power supplied to them. No big enough battery was available and power had to be taken from the town mains—and the voltage on these mains varies widely. Floating batteries were arranged to steady the valve filament voltage, but the magnet circuit and the motor circuit (driving the 600-volt generator supplying the anode current) could not be dealt with in this way, and it was ultimately found necessary to make an automatic voltage regulator to keep the supply voltage steady. The regulator, which embodies several interesting devices, was made in the laboratory to the author's design and answered admirably.

Method of measuring the amplitude of oscillations.—It was not found possible to measure the amplitude of the oscillations by looking at the rod directly, either with front or back illumination; the rod presents too hazy an appearance. When the amplitude is less than the diameter of the rod and the light is behind it, the width of the dark central band, which is never uncovered, can be measured approximately, but small roughnesses in the rod as seen through the microscope prevent accurate measurements being obtained. If the rod is illuminated from the front and seen against a dark background, good measurement can be made if there is any bright speck on the surface of the rod. The bright speck appears elongated into a line whose length can be measured. After various trials a most successful method was found for making a very bright spot of minute dimensions. A bead of gold, formed by fusing the end of a 40 S.W.G. wire, was stuck on the rod. A 2-volt lamp of small size was fixed about 8 inches away, and its image in the bead formed a brilliant spot, so small as to have no appreciable size even when seen under a magnification of 150 diameters in the measuring microscope. When the rod oscillates this spot forms a bright line whose length is easily measured accurately.

Balancing the trunnions.—The mass of the trunnions and the stiffness of the torsion wires both introduce small errors, which are of opposite sign, so that it was possible to adjust them so that the errors cancelled. To do this it was only necessary to make the natural period of torsional oscillation of the trunnions supported by the torsion wires alone (no test piece being in them) equal to the natural period of the bar. The stiffness of the wires was found experimentally by putting a short iron rod in a trial trunnion and causing it to oscillate by means of a little electromagnet excited with alternating current. The required size of the trunnion was then calculated and the new trunnions mounted. These were then tested in the same way and tuned to the exact speed by adding small masses on the periphery, similar to the weights on a watch-balance. For the highest speed rather stiffer wires were used than for the others.

Materials tested.—The only three materials tested were copper, Armco iron and mild steel. These materials were selected because most of the researches of the Fatigue Panel of the Aeronautical Research Committee had been carried out on them.

The copper was obtained in the form of wire 0·105 inch diam. The National Physical Laboratory analysed it with the following result :—

Copper, 99·97 per cent. ; Arsenic, nil ; Nickel, trace ; Oxygen, 0·03.

The wire was cut into lengths and carefully straightened by gentle blows with a wooden mallet, and then annealed for half-an-hour at 600° C. in an electric furnace. The straight rods were put in one limb of a hard glass U-tube, the other limb of which was filled with scrap copper wire. Dried hydrogen was passed very slowly through the tube as it lay in the furnace, entering by the side filled with scrap copper. At the end of the period the wires were drawn out of the U-tube and quenched in water. There were slight traces of oxidation in the first inch of the scrap wires, but none in the rest of their length or in the test pieces.

The Armco iron was obtained in the form of wire 0·104 inch diam. The National Physical Laboratory analysed it with the following result :—

Carbon, 0·05 per cent. ; Silicon, trace ; Sulphur, 0·010 ; Phosphorus, 0·016 ;
Manganese, 0·44 ; Nickel, 0·014 ; Chromium, trace ; Arsenic, 0·021 ;
Copper, 0·012.

It was cut into lengths and straightened like the copper and then normalized by heating for half-an-hour between 950° and 975° C. and then cooling in the air. The straight rods were put in a piece of iron gas-pipe with screwed caps and packed with kieselguhr. The whole was heated in an electric furnace and then taken out and allowed to cool. The rods when removed from the tube were found to be silvery grey, without signs of oxidation.

The mild steel was obtained in the form of wire 0·104 inch diam. It was analysed by Dr. L. Aitchison with the following result :—

Carbon, 0·27 per cent. ; Silicon, 0·10 ; Manganese, 0·74 ; Sulphur, 0·023 ;
Phosphorus, 0·034.

The wire was treated in the same way as the Armco iron, except that the normalizing temperature was between 850° and 880° C.

Testing Procedure.—Before any recorded tests were made, thorough trials were made to find out the most suitable adjustments in the electric circuits. Some of the samples used in these preliminary trials were tested to fracture, so that approximate values of the fatigue limit could be estimated before the recorded tests were begun. For each recorded test a fresh test piece was put into the

apparatus and quickly run up to the selected amplitude, and then kept steady at that amplitude by slight adjustments when necessary. The run was then continued without interruption till fracture occurred (or till at least 10 million cycles had been completed). The low frequency tests at 50 cycles per second lasted 55 hours or less, the tests at 500 periods lasted $5\frac{1}{2}$ hours or less, and the tests at 1,000 lasted $2\frac{3}{4}$ hours or less, and the fastest (2000 cycles) lasted 83 minutes or less. The Armco iron and steel samples failed very suddenly, but the copper samples much more gradually.

The first sign of failure was the reduction of amplitude, owing to the increase in the natural period of vibration of the test piece. When the apparatus was re-tuned it quickly went out of tune again, and was then stopped and the crack found. An interesting feature of the tests in this apparatus is that complete fracture rarely occurs, the specimen automatically comes practically to rest as soon as a serious crack has developed. This is in striking contrast to what occurs in the ordinary testing machines; in these it is extremely difficult to catch a crack before complete fracture.

Results of the Tests.—The results are given in Tables I, II, III, and plotted in the accompanying diagrams (graphs A—E).

Table I.—Copper.

Sample number.	Periods per sec.	Apparent $E \times 10^6$.	Strain $\times 10^{-8}$.	Duration $\times 10^6$.	Result.
2	975	16.55	33.32	5.85	Broken.
3	986	17.05	30.10	9.76	Unbroken.
5	970	16.40	30.52	12.7	„ Fatigue limit strain, 32.5×10^{-8}
6	971	16.5	30.73	20.4	„ „ „ stress, tons per sq. in.
7	968	16.3	31.50	11.6	„ (using $E = 16.4 \times 10^6$) 5.33.
8	971	16.4	31.85	11.4	„ Mean apparent $E = 16.4 \times 10^6$.
9	972	16.4	32.62	9.9	Broken.
10	969	16.3	32.41	12.6	Unbroken.
11	970	16.35	32.34	10.8	„
15	505.0	15.9	32.76	13.2	Broken.
16	506.0	16.0	32.62	10.0	„ Fatigue limit strain, 31.74×10^{-8} .
17	507.5	16.2	32.06	11.9	„ „ „ stress, 5.01.
18	500.5	15.6	31.78	9.54	„ (using $E = 16.4 \times 10^6$).
19	501.5	15.6	31.22	15.3	Unbroken. Mean apparent $E = 15.8 \times 10^6$.
20	502.0	15.6	31.50	13.7	„
21	510.5	16.0	31.71	15.2	„
1	50.2	15.45	31.99	4.52	Broken. Fatigue limit strain, 29.8×10^{-8} .
2	50.5	15.50	30.59	6.46	„ „ „ stress, 4.88.
3	50.3	15.45	29.95	8.52	„ (using $E = 16.4 \times 10^6$).
4	50.3	15.45	29.95	6.90	„ Mean apparent $E = 15.45 \times 10^6$.
24	1,960	16.3	38.7	1.88	Broken. Fatigue limit strain, 33.7×10^{-8} .
25	1,980	16.6	34.2	8.09	„ „ „ stress, 5.53
26	2,000	16.8	33.9	9.0	„ (using $E = 16.4 \times 10^6$).
27	2,010	16.8	33.6	10.8	Unbroken. Mean apparent $E = 16.6 \times 10^6$.

Table II.—Armco Iron.

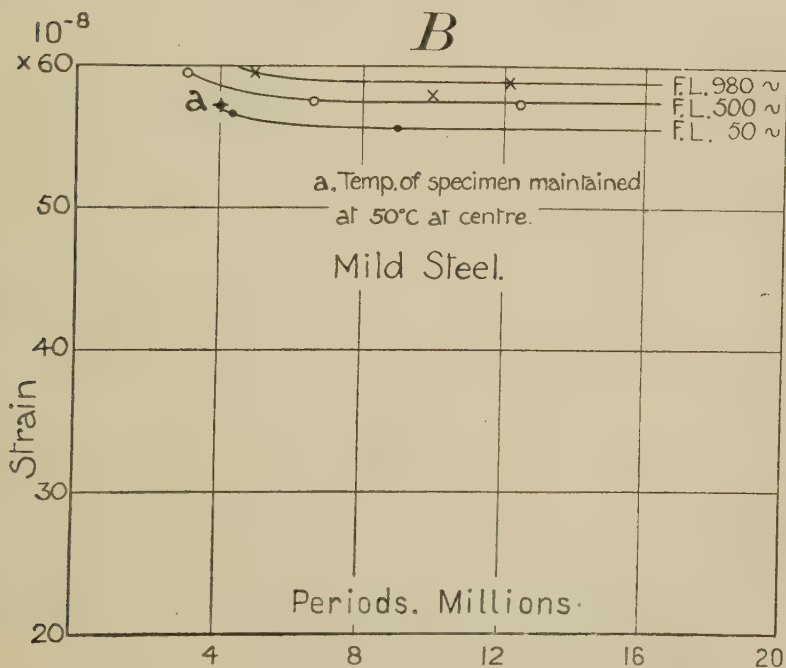
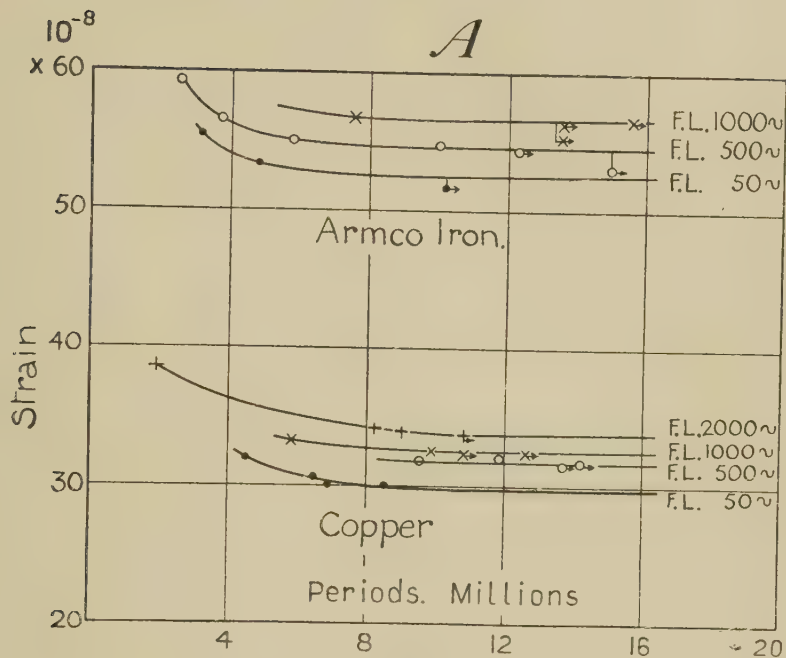
Sample number.	Periods per sec.	Apparent $E \times 10^6$.	Strain $\times 10^{-8}$.	Duration $\times 10^6$.	Result.
5	1,009	30.2	55.23	13.6	Unbroken. Fatigue limit strain, 56.6×10^{-8} .
8	1,002	30.0	56.77	7.53	Broken. " " stress, 16.98.
9	1,002	30.0	56.21	13.55	Unbroken (using $E = 30 \times 10^6$).
12	1,001	30.0	56.42	15.62	" Mean $E = 30.1 \times 10^6$.
2	500.0	30.4	59.29	2.55	Broken. Fatigue limit strain, 54.5×10^{-8} .
3	500.5	30.3	56.49	3.76	" " stress, 16.65.
4	500.5	30.3	52.99	15.0	Unbroken (using $E = 30 \times 10^6$).
6	505.0	30.8	54.32	12.3	" Mean $E = 30.4 \times 10^6$.
7	504.0	30.6	54.95	5.8	Broken.
11	500.0	30.3	54.67	10.02	"
13	50.0	30.0	51.6	10.2	Unbroken. Fatigue limit strain, 52.5×10^{-8} .
14	50.2	30.2	55.4	3.16	Broken. " " stress, 15.75.
15	49.6	29.7	53.3	4.8	" (using $E = 30 \times 10^6$).
16	50.0	30.0	52.7	6.9	" Mean $E = 30.0 \times 10^6$.

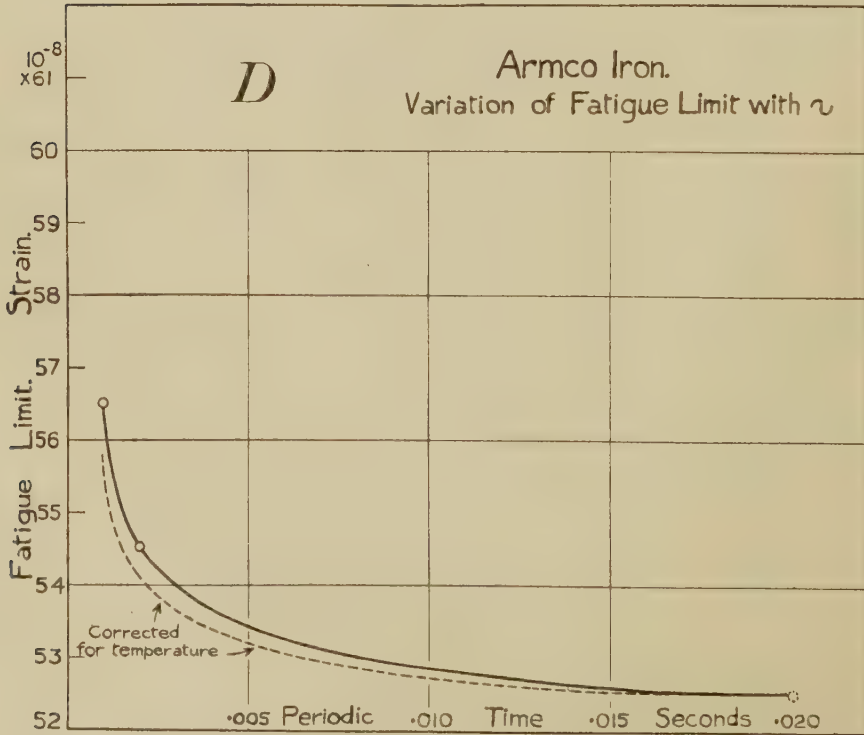
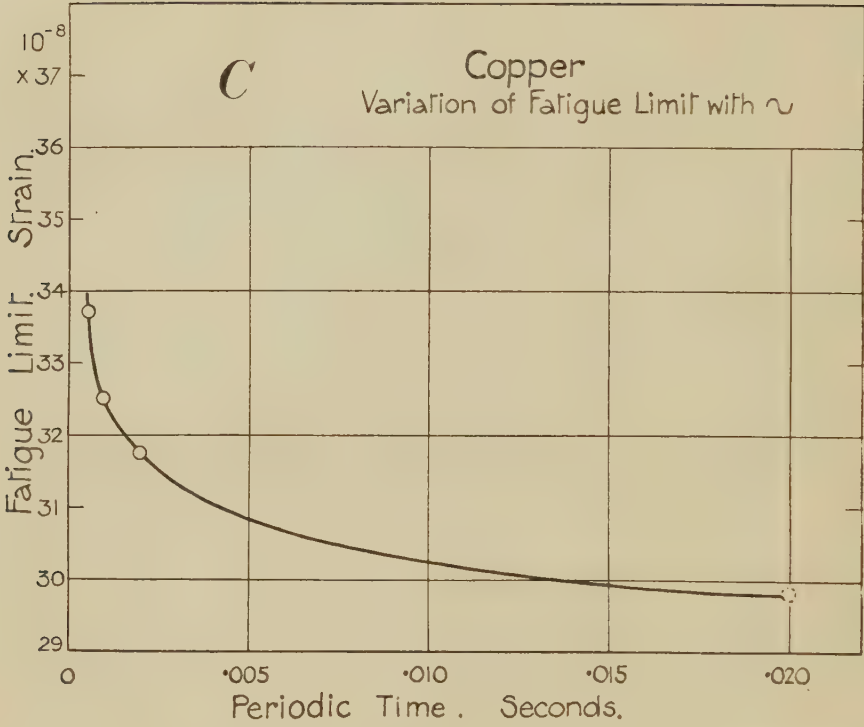
Armco with Cold Air Blast.

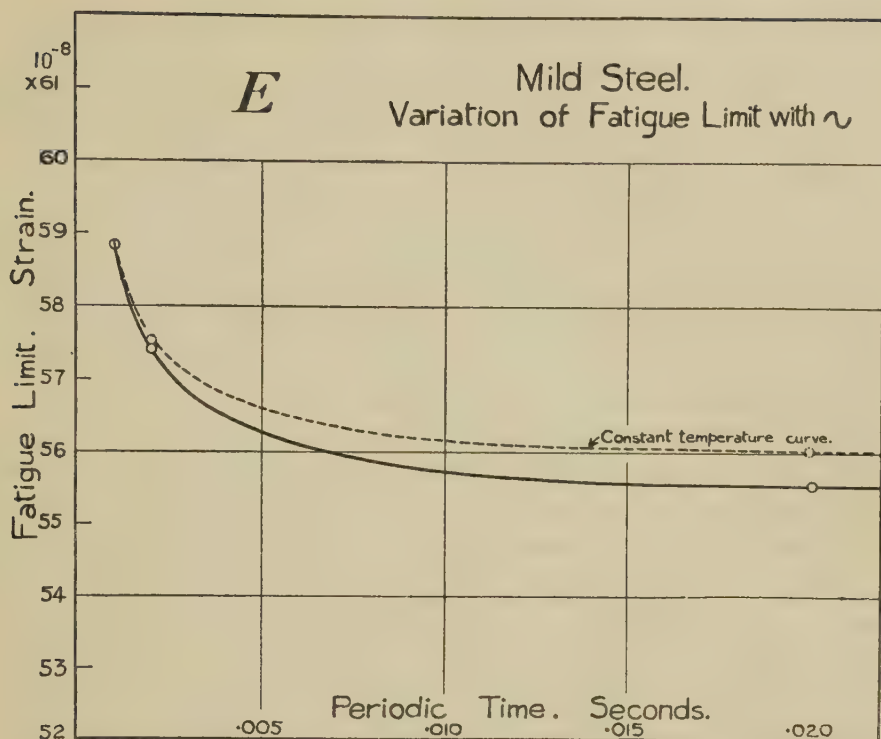
17	980	29.8	55.5	12.5	Unbroken. Fatigue limit strain, 55.9×10^{-8} .
18	980	29.8	56.0	8.0	Broken. " " stress ($E=30$), 16.8 tons/sq.in.
					Mean $E = 29.8$.

Table III.—Mild Steel.

Sample number.	Periods per sec.	Apparent $E \times 10^6$.	Strain $\times 10^{-8}$.	Duration $\times 10^6$.	Result.
2	980	29.4	59.5	5.0	Broken. Fatigue limit strain, 59.0×10^{-8} .
3	978	29.4	58.0	10.0	Unbroken. " " (using $E = 29.4$), 17.35 tons/sq. in.
4	976	29.3	58.8	12.2	Unbroken. Mean $E = 29.4 \times 10^6$.
5	495	29.4	59.5	3.1	Broken. Fatigue limit strain, 57.4×10^{-8} .
6	502	30.2	57.5	6.65	Broken. " " stress ($E = 29.4$) 16.85.
7	497	29.6	57.3	12.5	Unbroken. Mean $E = 29.7 \times 10^6$.
9	49.6	29.5	56.6	4.38	Broken. Fatigue limit strain, 55.5×10^{-8} .
12	49.5	29.5	55.6	9.0	" " stress ($E = 29.4$) 16.3.
					Mean $E = 29.5 \times 10^6$.
At 50° C.					
13	49.8	29.7	57.25	4.05	Broken.







The strains are calculated from equation 13 in the Appendix (p. 142). From this equation the maximum strain in each test piece was calculated and the results are given in terms of strain. But fatigue limits are commonly expressed in terms of stress, not strain, the stress being calculated from the strain on the assumption that the metal is elastic. This assumption is approximately true for steels at ordinary temperatures, but is far from true for steels at higher temperatures and for copper and Armco iron at ordinary temperatures. In all these metals the fatigue limit is much higher than the elastic limit. For the convenience of those who are more familiar with the ordinary method of expressing the results, the stresses corresponding to the strains have been calculated in the ordinary way and are given in the tables. To make these calculations some value of Young's modulus E has to be assumed. The experiments themselves enable a value of E to be calculated, for the mass of the test piece and its period of vibration are known. The values of E calculated from these data are not real constants of the material, even under the particular conditions of test, but represent special average values for the whole of each bar, which is subject to stresses varying along its length and also from its axis

to its surface. These values of E are tabulated and a suitable value is chosen for calculating the stress.

The results of the tests were very concordant; when plotted in the usual way—strain against number of alternations to fracture—they lie very closely on smooth curves (see graphs A—B).

Corrections for the Rise of Temperature of the Test Piece.—During the discussion on the results of the tests it was suggested that the apparent rise of the fatigue limit might be due to a rise of temperature—the test piece would certainly heat more at the higher frequencies. A special investigation was therefore made to determine what temperatures were actually reached and what effect a rise of temperature might have on the fatigue limit.

To measure the temperatures, thermo-junctions of 40-gauge wire were soldered to the test pieces, which were then run under the same conditions as the fatigue tests. The copper test pieces never rose more than 8°C . above atmosphere, and it was assumed that this small rise could have little effect on the fatigue limit. The Armco iron test piece, however, was found to be 40°C . hotter at the maximum speed (1000 $\curvearrowright$) than at 50 $\curvearrowright$. In order to ascertain the probable effect of this difference of temperature a fresh determination of the fatigue limit was made when the sample was kept much cooler by means of a blast of air. The air reduced the maximum rise of temperature to one-quarter what it was before, and the fatigue limit strain was 55.9×10^{-8} . From this result it is estimated that the fatigue-limit strain would have been 55.7×10^{-8} if there had been no temperature rise. Graph D shows the approximate curve for the rise of the fatigue limit with frequency after making this temperature correction.

The temperature of the mild-steel specimens was found to be about 50°C . at 1,000 $\curvearrowright$. A different method of allowing for the difference of temperature was employed. A hot-air blast was used to warm up the test piece running at 50 $\curvearrowright$ to the same temperature (50°) as the high-speed one. The air was warmed by passing it through a silica tube containing an electrically-heated coil, and was blown through a light wooden box fitted round the test piece. The air blast was started and the temperature adjusted several hours before the fatigue test began. The temperature was measured again at the end of the test and was found to be unaltered. A single test only was made. The sample broke, after 4 million cycles, as is shown by the point a in graph B. This point lies 0.5 units above the curve for the cold tests, and it is assumed that the F.L. is also 0.5 units above that for the cold tests. The curve corrected in this way is shown dotted in graph E (the correction was not determined for 500 $\curvearrowright$).

The temperature corrections determined in these ways are clearly not very accurate. Greater accuracy was not attempted, because it was hoped that the new torsion apparatus, intended to give results up to 5,000 $\sim$, would enable tests to be made at constant temperatures. Unfortunately, as is explained later, this apparatus was not successful.

The results confirm Hopkinson's anticipation, but show that effect of speed is very much less than was suggested by his experiments. From the user's point of view they show that materials (so far as they are similar to those tested) gain slightly in their strength to resist fatigue as the speed goes up, but for most practical speeds the gain is insignificant. The effect of speed of testing on the results is also insignificant at any of the ordinary speeds. It has often been suggested that vibration in the testing machine might falsify the results. The results of the present experiments show that high-frequency vibrations superposed on the ordinary load will not have any serious effect, due to their high frequency, but that their effect may be estimated simply from the additional load they cause in the test piece.

The results show that the mechanism of fatigue requires time. At high speeds the loads which are sufficient to cause fracture have not time to produce the effect, whatever it may be, which causes fracture, and higher loads are needed to produce the same effect. Any theory proposed to explain the mechanism of fatigue must account for this time-effect.

PART II.

The results obtained with the apparatus described in Part I of this paper showed that much more striking results were to be expected if the speed of alternation could be still further increased. This was not possible in the original apparatus. As the speed is increased, the length of the sample has to be reduced, and the amplitude gets smaller, till it is no longer possible to do the necessary work on the sample by the electromagnetic forces. In the 2000 $\sim$ tests the magnetic field was only 1 inch wide, and the amplitude of vibration at the centre of the test piece was only 0.08 mm. Under these conditions the Armco iron and steel could not be broken; the copper sample was the only one broken at that speed. To get higher speeds some other method of producing oscillations had to be devised.

It appeared possible that torsion tests could be carried to higher frequencies, and an apparatus was designed to work up to 5000 $\sim$. The arrangement of the apparatus is shown in fig. 3. The test piece consists of a straight vertical rod (or later a tube) fixed at its upper end (in the simplest design) and fitted

at the lower end with a very small cross-bar armature of soft iron which hangs between the poles of an electro magnet, in such a position that when the

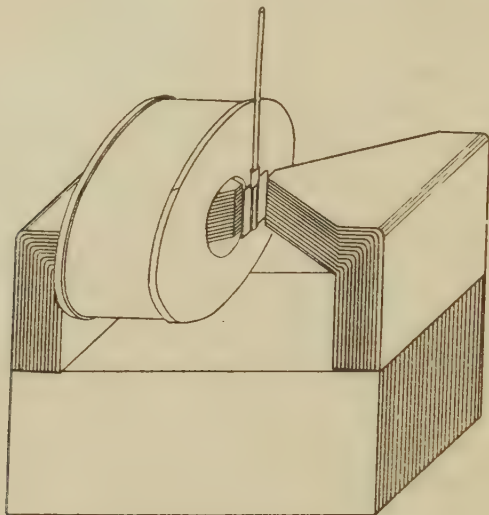


FIG. 3.

magnet is excited the test piece is twisted. The twist is measured by a small mirror, 3 mm. $\times$ 1 mm., stuck on the test piece just above the iron armature. The magnet is laminated and is fitted with coils over the poles; it is excited as in the earlier experiments by an alternating current derived from an oscillating circuit turned to the natural period of torsional oscillations in the test piece. The test piece is threaded through a hole in a small bracket just above the armature, which acts as a steady to keep the armature central in the field.

Arranged in this way the apparatus has the common defect referred to in Part I, that the stress in the test piece is a maximum at the point of fixture, so that a machined test piece would have to be used with a thick end for gripping. This defect can be got over by using a test piece three times as long. This will oscillate with nodes at the top and two-thirds down and the stress will be a maximum at these points. If the top one-third be made of thinner rod the actual stress at its point of fixture at the top will be less than in the thicker rod in the ratio of the diameters, thus the fracture will occur at the lower node and not at the top. A sample of this type was made and tested, and vibrations of the type desired were produced.

Armature Design.—The crucial difficulty in the apparatus is the design of the armature. It must be large enough to give the necessary power, but its polar

moment of inertia must be very small. A rod of copper 4.4 inches long oscillates torsionally at 5,000 ω (the frequency is independent of the diameter). If the frequency is to be maintained when the armature is attached, the rod must be shortened by a length whose polar moment of inertia is roughly equal to the polar moment of inertia of the armature. Shortening the rod has two serious disadvantages, it reduces the length on which the twist can be measured (this can be got over, by using the long test piece described above) and it increases the torsional stresses in the armature attachment. The torsional stress in the rod varies according to a cosine law from zero at the free end to a maximum at the fixed end. If the armature has an equivalent length equal to half the length of the bar, then the stress at the point of attachment will be about seven-tenths of the maximum stress, *i.e.*, of the breaking stress, when a test is being run. This makes the design of the attachment very difficult.

Many designs were prepared for armatures and several were made and tried. More than one of these enabled an amplitude estimated to be sufficient to break the test piece to be reached, but the estimate was too low and it was found impossible to make an armature powerful enough to break the test piece. As has been already stated the moment of inertia of the armature must not exceed that of about 2 in. of the test piece. The diameter of the test piece must be kept small or the angle of the twist becomes so small that the necessary work cannot be done by the magnetic couple. The body of the armature must be non-magnetic and have a high specific resistance, to keep down eddy currents, and for the same reason it should not surround the iron core. The centre of gravity of the armature must lie on the axis of rotation.

All these conditions have been fulfilled in the two designs shown in figs. 4 and 5. Non-magnetic steel (kindly furnished for these experiments by Dr. W. H. Hatfield) and Manganin were tried for the body. The first iron core was made of iron wires (first round, then square) filed to a wedge-shape at the ends and soldered on. This design reduces eddy currents to a minimum—but the solder broke. A flat sheet of Stalloy was then used: this did not heat, but again broke off. At this stage it was found necessary to use a hollow test piece with water cooling, and the armature shown in fig. 5 was made. Two thin sheets of Stalloy, grooved in the centre, were brazed in a non-magnetic steel sleeve, and this design was used up to the end. It does not appear to be possible to reduce the inertia any further.

The design of the magnet also required much consideration. The poles have to come very close together, but leakage of flux must be minimised. In the first magnet tried the hysteresis loss was large and the inductance of the

coils excessive. The final design is shown in fig. 3 above. The magnets are built up of stampings of Permalloy, kindly given for the purpose by the Research

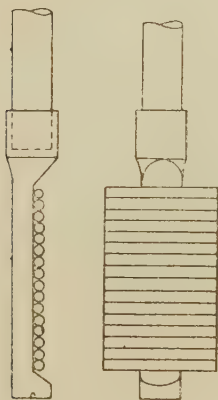


FIG. 4.

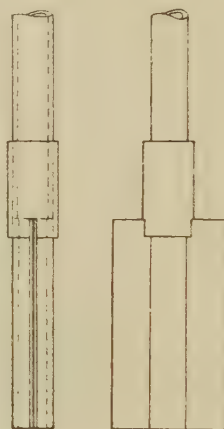


FIG. 5.

Department of the General Electric Company of America; they were heat treated after bending. The poles are tapered down sharply from the large section in the yoke. The coils are wound on conical bobbins so as to concentrate the winding as near the air gaps as possible and so reduce their inductance and the leakage flux. The inductance can be compensated for entirely by putting a condenser in parallel; the arrangement of the circuit shown in fig. 6 has an equivalent effect and is simpler. The coils had several taps, but the number of turns used was found not to matter much.

The oscillating circuits are shown in fig. 6. The current taken from the induction coil is passed directly into the coils on the magnets—no transformer is needed. To cancel the inductance of the magnet coils a variable capacity was placed in parallel with them, and as this capacity can be used for tuning, the original tuning capacity was removed, so that there were left only two taps, instead of three, on the induction coil. This arrangement allowed a much larger current to circulate in the magnet bobbins than was taken from the induction coil. The rest of the apparatus is the same as was used in the earlier tests.

Amplitude and Frequency Measurements.—After various trials the arrangements shown in figs. 7 and 8 were adopted for measuring the amplitude of the

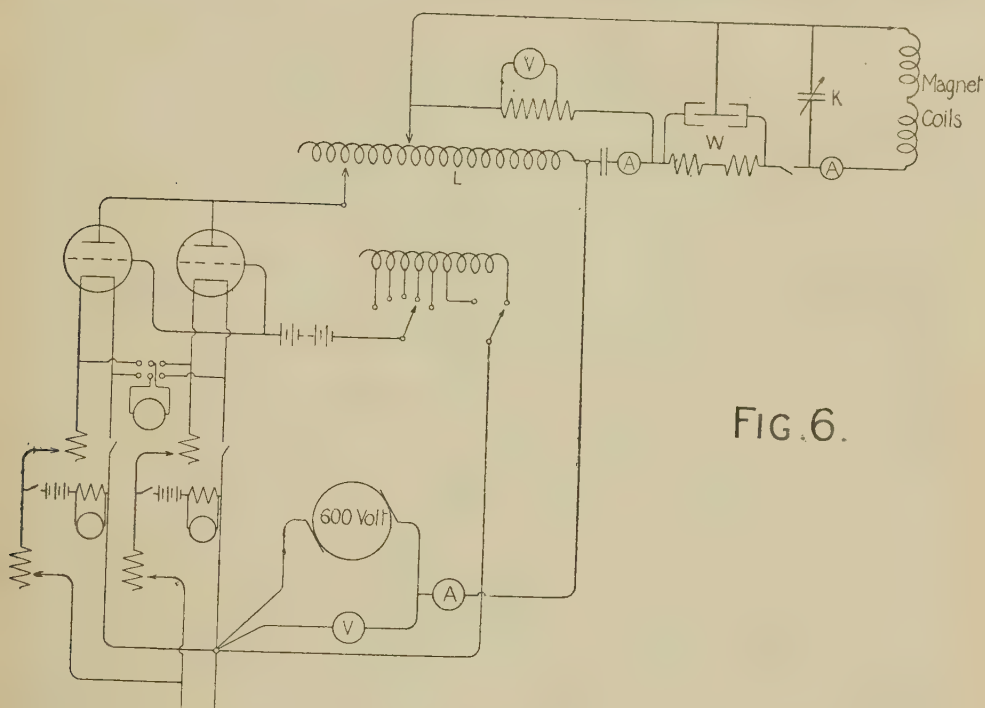


FIG. 6.

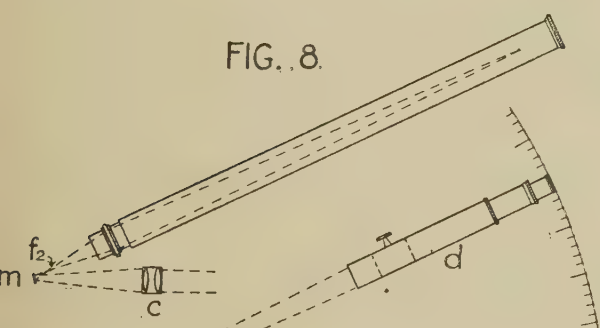


FIG. 7

torsional vibrations, and answered satisfactorily. A 4-volt straight filament lamp was mounted with the filament vertical at *a*, just behind the stroboscope

disc *b*. The light from this was focused by the photographic lens *c*, at a point f_1 just in front of the mirror *m* on the test piece. The image of this point of light in the mirror was observed through the swinging telescope *d*, which has a vertical hair line in the eye-piece. The angular deflection of the mirror was measured by swinging the telescope round its pivot, fixed exactly under the test piece, till the end of the band of light coincided with the hair line. The angle of swing of the telescope from one end to the other of band of light was read on a horizontal scale on the table supporting the telescope. The stroboscope disc was stationary during these measurements.

For making stroboscopic observations the lens *c* was slid forward about an inch, so as to focus the light at f_2 (fig. 8) after reflection in the mirror. The telescope was removed and a special microscope substituted, by which the whole travel of the spot of light at f_2 could be seen in the field of view at one time. The object-glass of this special microscope is a 3-inch cinema photograph lens of wide aperture ($f/3$). The object-glass and eye-piece are mounted in a paper tube. The length of travel of the spot of light f_2 can be adjusted so as to be a convenient length for viewing in this microscope by adjusting the position of the lens *c*. The microscope is focused by sliding the whole tube nearer or farther from the spot f_2 . After a little practice the stroboscope speed could be quickly adjusted to give an almost stationary spot of light as seen in the microscope. The stroboscope disc had 100 holes 0.02-inch diameter. Both arrangements gave bright enough illumination to be used in daylight when the laboratory blinds were half down. For rough measurements of angle of twist it was found to be satisfactory to omit the lens *C*, and to put the lamp about 6 inches in front of the mirror and view its image through the swinging telescope.

Results.—As has already been stated, no test pieces were broken with this apparatus. The following tables give the results of the three best tests, *i.e.*, those in which the largest strains were reached :—

(1) Test piece, copper tube ; outside diameter, 0.104 in. ; bore, 0.078 in.

Effective length, fixed point to mirror, 0.85 in.

Telescope angular swing, 4.8° .

Twist of mirror $\pm 1.2^\circ$.

Strain, 0.00129. Approx. stress, 3.68 tons/sq. in.

Unbroken after 60×10^6 periods.

Frequency, 4,000 periods per second.

The bending fatigue limit for copper at a frequency of 2,000 was 5.67

tons/sq. in. Thus in this test the torsional stress reached 0.65 times the tension stress sufficient to cause fracture at 2,000 periods.

(2) Test piece, copper tube, as above.

Effective length, fixed point to mirror, 3.25 in.

Telescope angular swing, 17.0°.

Twist of mirror, $\pm 4.25^\circ$

Strain, 0.00119. Approx. stress, 3.39 tons/sq. in.

Unbroken after more than 10×10^6 periods.

Frequency about 3,000 periods per sec.

Stress = 0.6 times the fatigue limit of copper in tension at 2,000 periods.

(3) Test piece, copper rod; outside diameter, 0.106 in.

Effective length, 3.0 in.

Telescope angular swing, 15°.

Twist of mirror $\pm 3.75^\circ$.

Strain, 0.00118. Approx. stress, 3.35 tons per sq. in.

Unbroken after 25×10^6 periods.

Frequency about 3,000 periods per second.

The temperature of the test piece rose about 100° C.

These results show that the apparatus was not powerful enough to overcome the large hysteresis which appears as the fatigue limit is closely approached. The power appeared to be limited by the magnetic saturation of the iron in the armature. Attempts were made to measure the magnetic flux in the armature by winding a search coil round it, but the results were unreliable, because the coil was necessarily considerably larger than the iron and the leakage flux in the air was large. All attempts to get larger twists were fruitless and the experiments had to be abandoned.

The author has to acknowledge the great assistance he received in making these experiments from his assistants, Mr. D. M. D. Brunyate and Mr. G. Y. Hemingway.

APPENDIX.

Vibration of a Beam supported at the Nodes with Free Ends.

The equation of motion is

$$\frac{d^4 y}{dx^4} + \frac{w}{gEI} \cdot \frac{d^2 y}{dt^2} = 0. \quad (1)^*$$

* Morley, 'Strength of Materials,' Chap. XIV.

Assume the vibration to be simple-harmonic with respect to time, then, if y_m = maximum value of y at a given point in the beam,

$$y = y_m \cdot \cos \left(m^2 \cdot \sqrt{\frac{EgI}{w}} \cdot t \right) \quad (2)$$

where m is a constant of dimensions $(L)^{-1}$.

If then N = frequency of bar in periods per second, we have

$$N = \frac{m^2}{2\pi} \cdot \sqrt{\frac{gEI}{w}} \quad (3)$$

where w = weight of the beam per unit length.

y = deflexion of the beam from equilibrium position.

x = distance measured along the beam from an arbitrary origin.

E = Young's Modulus for the beam.

I = moment of inertia of the cross-section of the beam about the neutral axis.

g = acceleration due to gravity.

Making the substitution (2) in equation (1), we have

$$\frac{d^4 y_m}{dx^4} \cdot \cos \left(m^2 \sqrt{\frac{gEI}{w}} \cdot t \right) - \frac{wy_m}{gEI} \cdot m^4 \cdot \frac{gEI}{w} \cdot \cos \left(m^2 \sqrt{\frac{gEI}{w}} \cdot t \right) = 0,$$

or

$$\frac{d^4 y_m}{dx^4} - m^4 \cdot y_m = 0,$$

giving

$$y_m = A \cdot \cos(mx) + B \cdot \sin(mx) + C \cdot \cosh(mx) + D \cdot \sinh(mx). \quad (4)$$

Let now l = whole length of the beam, and

$2r$ = distance between the nodes.

Take the origin of co-ordinates at the centre of the beam when at rest. Since the supports are at the nodes, there will be no dynamic force acting there, and one equation will hold good for the whole beam. When $-x$ is substituted for x , y_m is unaltered.

Hence

$$B = D = 0. \quad (5)$$

When $x = r$, $y_m = 0$. Hence

$$A \cdot \cos(mr) + C \cdot \cosh(mr) = 0. \quad (a)$$

When

$$x = \frac{l}{2}, \quad \frac{d^2 y_m}{dx^2} = 0. \quad \text{Hence}$$

$$-A \cdot \cos\left(\frac{ml}{2}\right) - C \cdot \cosh\left(\frac{ml}{2}\right) = 0, \quad (b)$$

and, since there are no reactions, the C.G. does not move,

hence
$$\int_{-l/2}^{l/2} wy \cdot dx = 0,$$

i.e.,
$$A \cdot \sin\left(\frac{ml}{2}\right) + C \cdot \sinh\left(\frac{ml}{2}\right) = 0. \quad (c)$$

From (a) and (b)

$$C \left\{ \cosh (mr) \cdot \cos \left(\frac{ml}{2} \right) + \cosh \left(\frac{ml}{2} \right) \cdot \cos (mr) \right\} = 0,$$

$$A \left\{ \cos (mr) \cdot \cosh \left(\frac{ml}{2} \right) + \cosh (mr) \cdot \cos \left(\frac{ml}{2} \right) \right\} = 0.$$

Hence, rejecting the solution $A = C = 0$, we have

$$\cosh (mr) \cdot \cos \left(\frac{ml}{2} \right) + \cosh \left(\frac{ml}{2} \right) \cdot \cos (mr) = 0. \quad (6)$$

From (b) and (c),

$$\tanh \left(\frac{ml}{2} \right) = -\tan \left(\frac{ml}{2} \right).$$

Approximate solutions are $\frac{ml}{2} = \frac{3\pi}{4}, \frac{7\pi}{4}$, etc.

The lowest speed of vibrations gives

$$m = \frac{3\pi}{2l} \text{ approximately.} \quad (7)$$

A more accurate solution is

$$\frac{ml}{2} = 2.365 \text{ radians} = 135^\circ 31' 30'' \quad (7a)$$

giving m .

To get the ratio of r to l we have

$$\cosh (mr) \cdot \cos (2.365) + \cos (mr) \cdot \cosh (2.365) = 0,$$

i.e.,
$$\cosh (mr) = \cos (mr) \times \sqrt{2} \left\{ \frac{10.5 + \frac{1}{10.5}}{2} \right\}; \quad (10.5 = e^{2.365}),$$

or
$$\cosh (mr) = \cos (mr) \times 7.46. \quad (8)$$

The solution of this is $mr = 1.302$ radians.

So
$$r = \frac{1.302}{m} = 0.2754 \times l. \quad (9)$$

This checks well with Kaye and Laby's figure, $r = 0.276 \times l$, and Lord Rayleigh's figure, $r = 0.2758 \times l$.

To obtain the stresses in the beam, we have

$$y_m = A \cdot \cos (mx) + C \cdot \cosh (mx), \quad (4)$$

and
$$A \cdot \sin \left(\frac{ml}{2} \right) + C \cdot \sinh \left(\frac{ml}{2} \right) = 0, \quad (c)$$

where $\frac{1}{2}(ml) = 2.365$ radians.

From the tables, $A \times 0.7001 + C \times 5.248 = 0$,

or
$$A = -7.49 \cdot C. \quad (10)$$

Let R be the extreme fibre strain in the beam,

then
$$I \cdot \frac{d^2 y_m}{dx^2} = M = \frac{2RI}{d}, \quad \text{or} \quad \frac{d^2 y_m}{dx^2} = \frac{2R}{d}.$$

So
$$\frac{2R}{d} = -Am^2 \cdot \cos (mx) + Cm^2 \cdot \cosh (mx). \quad (11)$$

If now $\frac{d^2 y_m}{dx^2}$ is a maximum, $\frac{d^3 y_m}{dx^3} = 0$,

i.e.,
$$Am^3 \cdot \sin (mx) + Cm^3 \cdot \sinh (mx) = 0,$$

giving either $x = 0$, which is at the centre of the beam, or

$$\frac{\sin (mx)}{\sinh (mx)} = -\frac{C}{A} = 0.1335,$$

which is at the end of the beam. But the B.M. at the end of the beam cannot be a maximum, hence this solution gives a minimum, and the only maximum is at the centre of the beam. Hence

$$\frac{2R_m}{d} = -Am^2 + Cm^2 = 8.49 \cdot Cm^2.$$

Whence
$$C = \frac{2R_m}{d \cdot m^2 \cdot (8.49)} \quad \text{and} \quad A = -\frac{2R_m (7.49)}{d \cdot m^2 (8.49)},$$

R_m being the maximum fibre strain at the centre of the beam.

Hence $y_m = A + C = -6.49 \cdot C$, where y_m is the maximum value of y , which will clearly be at the centre, where $x = 0$.

Hence the central amplitude will be given by

$$a = \frac{2R_m (6.49)}{d \cdot m^2 (8.49)}, \quad (12)$$

or
$$R_m = \frac{adm^2 (8.49)}{12.98}. \quad (13)$$

At the end, the amplitude a_e is given by

$$\begin{aligned}a_e &= A \cdot \cos (2 \cdot 365) + C \cdot \cosh (2 \cdot 365) \\&= C (-7 \cdot 49 \times -0 \cdot 7136 + 5 \cdot 343) \\&= 10 \cdot 69 \cdot C.\end{aligned}\tag{14}$$

Thus, the ratio of the amplitude at the end to the amplitude at the centre is given by

$$\frac{a_e}{a} = \frac{10 \cdot 69}{6 \cdot 49} = 1 \cdot 65.$$

This checks with Lord Rayleigh's figure of 1.6452.

Tensile Tests of Crystals of an Aluminium Zinc Alloy.

By C. F. ELAM, M.A., Armourers and Brasiers Research Fellow.

(Communicated by Professor H. C. H. Carpenter, F.R.S.—Received 29 May, 1925.)

By the method of straining and heat treatment* large crystals were grown in an alloy of aluminium containing 18.6 per cent. zinc. This alloy is very near the limit of solubility of zinc in aluminium, but the microstructure showed it to be a solid solution. The most favourable extension was 1 per cent., with a load of 12.2 tons per square inch. The crystals were not so large as those obtained for pure aluminium, rarely exceeding 2 inches in length and 0.5 inch in diameter. They were frequently covered with a surface layer of smaller crystals of varying size. These were removed by machining. Small test pieces were made varying in length from 1 to 2 inches over the parallel portion and having a diameter of from 0.05 to 0.25 inch.

The crystals gave excellent X-ray reflections. The structure appears to be similar to pure aluminium, but has a slightly larger lattice, viz., 4.18 Å compared with 4.06 Å for pure aluminium. Reflections from both cubic and octahedral planes were obtained. The angles calculated between each pair of planes showed that the crystals had cubic symmetry.

The positions of the crystal axes relative to the axes of the test piece were determined both before and after breaking the test pieces. These are shown in fig. 1. The method of obtaining this diagram has already been described.†

* Carpenter and Elam, 'Roy. Soc. Proc.,' A, vol. 100.

† G. I. Taylor and C. F. Elam, 'Roy. Soc. Proc.,' A, vol. 108, p. 30.

It represents part of the stereographic projection of the crystal axes, in which one of the cubic (100) axes is in the centre of the diagram and the four octa-

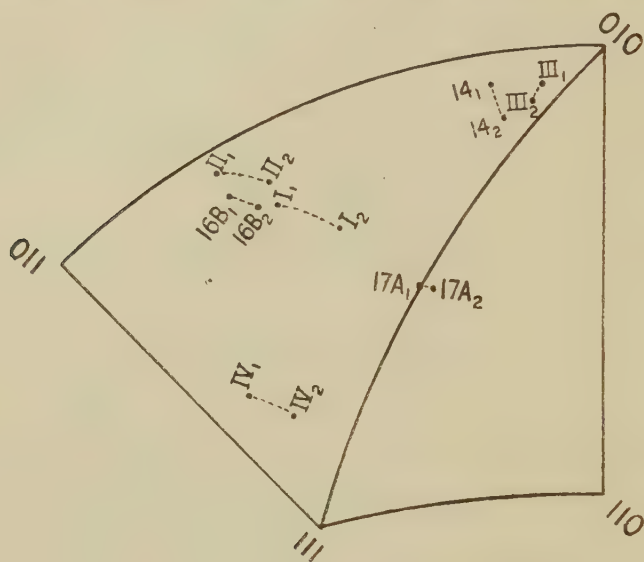


Fig. 1.

hedral (111) axes are arranged symmetrically round it. No distortion measurements were made on these crystals, but from a study of the movement of the axis relative to the crystal axes, and the appearance of slip-bands on the surface of the test piece, it appears as if slip occurred normally on an octahedral (111) plane in the (110) direction as in aluminium. The positions of the axis before and after stretching should lie on a great circle passing through the (110) axis towards which slip is taking place, while slip occurs on one octahedral plane, and fig. 1 shows that this is approximately the case. The test pieces were rather short, however, and there was local deformation near the fracture, so that errors in the X-ray measurements may account for some of the differences observed.

The figures for the tensile tests are given in Table I. Those for a normal bar of the same alloy, consisting of small crystals, are also given. There is considerable variation in the breaking loads for different crystals, and they fall, roughly, into two groups—one being about 16 tons to the square inch, the other being 20 to 21 tons to the square inch. All the figures for single crystals are higher than for the polycrystalline test piece.* This is particularly

* Cf. figures obtained by Rosenhain and Archbutt, 'Tenth Report to the Alloys Research Committee on the Alloys of Aluminium and Zinc.'

interesting in view of the opinion that is widely held that smallness of crystal size increases the strength of a material. The crystals have quite a definite yield-point at about 15 tons per square inch, which is accompanied by a drop in the beam. The elongations given are not indicative of the true extension of the metal, which was about 10–15 per cent., as some of these include the fracture, and the shortness of the test piece meant that the fracture occupied a larger proportion of the parallel portion than is normally the case.

On extending, the crystals became elliptical in cross-section, but did not elongate to the extent that the pure metal did. The fracture consisted of one principal cleavage plane, with a second plane, sometimes hardly noticeable, at approximately 90° to it. Both planes made angles of approximately 45° with the axis. It was found in the two cases examined that if a crystal boundary were included in the parallel portion of the test piece the fracture was intercrystalline. It seemed probable that, owing to the comparatively high annealing temperature (550° C.) to which these crystals were subjected, and the high volatility of the zinc, the crystal boundaries had been weakened, but the breaking load of these test pieces (Table I) was approximately the

Table I.—Tensile Strength of Alloy Crystals.

No.	Breaking load. Tons per square inch.	Elongation per cent.
16B	16·55	26
I	16·75	15
II	15·90	19
17A	20·01	18
III	21·70	10
14	20·30	20
IV	19·25	18
16A	16·45*	10*
17B	15·58*	4*
Normal bar	15·08	20

* Broke at crystal boundary.

same as for some of the single crystals, and actually exceeded that of the normal bar, which, although it also had been heated to 550° C., did not show intercrystalline fracture. Furthermore, heating *in vacuo* at 550° C. for six hours failed to remove any appreciable amount of zinc from this alloy.

Cleavage fractures somewhat similar to these are obtained when zinc* is

* H. Mark, M. Polanyi E. Schmid, 'Zeit. für Physik,' vol. 12 (1922).

broken at 190° absolute. Zinc has a hexagonal structure, and it was found by X-ray analysis that the fracture occurs on the basal plane in the cold, but that at ordinary temperatures it occurs on both the basal and pyramidal planes. An attempt was made to correlate the planes of fracture in this alloy with the crystallographic planes. This was found to be very difficult, owing to the local distortion of the crystal near the fracture, and to the fact that the planes of fracture were slightly curved. Furthermore, it was difficult to connect the positions of the fractures with the vertical lines ruled on the test pieces which were the reference lines for X-ray measurements. The results so far obtained are only approximate, and indicate in a general way some of the features of these crystals. In Table II are given a few measurements, which seem to show that the principal plane of fracture is very near an octahedral (111) plane in some cases, but that in others it is nearer a (112) plane. Where the fracture was near a (111) plane the line of greatest slope coincided with the minor axis of the ellipse (fig. 2). In the others the line of greatest slope was inclined to a more or less degree between the major and minor axis (figs. 3 and 4). These differences are due to the varying orientations of the bars.

Table II (A).—Angle between Normals of Planes of Fracture = 90° .

θ = angle between normal of plane and axis of test piece.

ψ = angle between reference plane in crystal, and plane containing normal, measured anti-clockwise.

No.	Principal fracture.	Nearest crystal plane.	Slip-bands.
I	$\theta = 44^\circ$ $\psi = 136^\circ$	$\theta_{111} = 50^\circ$ $\psi_{111} = 135^\circ$	Parallel to fracture, i.e. (111) plane.
II	$\theta = 48^\circ$ $\psi = 111^\circ$	$\theta_{111} = 46^\circ$ $\psi = 114^\circ$	Parallel to fracture, i.e. (111) plane.
16B	$\theta = 43^\circ$ $\psi = 12^\circ$	$\theta_{111} = 44^\circ$ $\psi = 8^\circ$	Parallel to fracture, i.e. (111) plane.
17A	$\theta = 43^\circ$ $\psi = 187^\circ$	$\theta_{112} = 44^\circ$ $\psi = 186^\circ$	Making small angle with fracture. $\theta_{111} = 59^\circ$. $\psi = 202^\circ$.
III	$\theta = 43^\circ$ $\psi = 182^\circ$	$\theta_{112} = 39^\circ$ $\psi = 183^\circ$	Making small angle with fracture. $\theta_{111} = 52^\circ$. $\psi = 198^\circ$.
14	$\theta = 41^\circ$ $\psi = 156^\circ$	$\theta_{112} = 39^\circ$ $\psi = 154^\circ$	Nearly perpendicular to fracture. $\theta_{111} = 53^\circ$. $\psi = 348^\circ$.

Table II (B).—Angle between Normals of Planes of Fracture = 120° .

No.	Fractures I and III.	Fracture II.	Nearest crystal plane.		Slip bands.
			Fractures I and III.	Fracture II.	
IV	$\theta = 45^\circ$ $\psi = 149^\circ$	$\theta = 29^\circ$ $\psi = 356^\circ$	(112) $\theta = 50^\circ$ $\psi = 161^\circ$	(112) $\theta = 31^\circ$ $\psi = 350^\circ$	Parallel to fractures I and III, <i>i.e.</i> (112). Perpendicular to fracture II. $\left. \begin{array}{l} \theta = 29^\circ \\ \psi = 191^\circ \end{array} \right\} (110) \text{ plane.}$

One crystal, No. IV, differed from any others in that there were three planes of fracture, of which the first and third were the same (fig. 5). The angle between the normal of these planes was roughly 120° , instead of 90° , and when these were compared with the figures obtained from the X-ray measurements they agreed approximately with two (112) planes.

Slip-bands were observed, which were sometimes parallel to the principal plane of fracture, and in all such specimens these agreed very nearly with the position of an octahedral plane. In others, there was a distinct difference in inclination between the slip-bands and the plane of fracture. (*See* figs. 3 and 4.) In one of these (No. 14, fig. 3) they were actually perpendicular to each other. This is confirmatory evidence that the plane of fracture is near a (112) plane in these crystals.

In No. IV slip-bands were observed parallel to two of the fractures, so that they were probably (112) planes, and also perpendicular to the other fracture, agreeing with a (110) plane.

Referring to fig. 1, it will be noticed that the type of fracture obtained depended on the original orientation of the crystal, and also that the breaking loads varied in the same way (Table I). No such differences in fracture were obtained with pure aluminium, nor were the breaking loads so variable. The orientation, however, affected the elongation, being greater the longer the slipping was confined to one plane.

In all the aluminium crystals examined the fracture consisted of a double-wedge, due to the fact that slip during the latter part of the extension occurred on two planes. No. 17A, fig. 4, showed a somewhat similar type of fracture, and it is interesting to note that the axis of this specimen was in such a position that if the same rules hold for the alloy as for the pure metal, it would be expected that double slipping could take place. This is further confirmed by

the very small change in position of the axis after an extension of 15 per cent. (fig. 1).

The small subsidiary planes of fracture were too small to measure, but the



FIG. 2.—No. 16B.



FIG. 3.—No. 14.



FIG. 4.—No. 17A.



FIG. 5.—No. IV.

fact that they were always present suggests that the distortion at the point of fracture was not always confined to one plane. The data at present available, however, are insufficient to enable any conclusions to be drawn on the subject.

Conclusions.

The results so far obtained show that the addition of 18 per cent. of zinc to aluminium does not destroy the cubic symmetry of the crystal. The hardness is very much increased and the amount of slip that can occur before fracture is much reduced. The orientation of the crystal relative to the axis of the test piece affects the breaking stress and the type of fracture. Fracture occurs on planes nearly at 45° to the axis, *i.e.*, on the plane of maximum shear. Fracture may occur along the slip-plane, but not always. The tenacity of the single crystals appears to be higher than that of the polycrystalline material.

These results are admittedly of only a preliminary nature, but they are interesting as showing the effect of alloying, and when larger crystals are available a more thorough investigation will be made.

The author is indebted to Prof. H. C. H. Carpenter, F.R.S., for his help and advice, and to the Government Grant Committee of the Royal Society for assistance in procuring apparatus, which has enabled this work to be carried out.

The Scattering of Light by Liquid Boundaries and its Relation to Surface Tension.—Part II.

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1. *Introduction.*

In the first paper, a description was given of the scattering of light by *metallic* liquid surfaces, particularly of the manner in which the intensity and state of polarisation of the scattered rays vary with the angle of incidence of the primary rays and the direction of observation. We now proceed to consider the phenomena observed when the clean and dust-free surface of a *transparent* liquid is strongly illuminated. Whereas in the case of metals we have a very few substances which are liquid at ordinary temperatures, an enormous variety of transparent liquids is available for the purpose of the present study. In fact, at the time the investigation was taken up, an extensive collection of pure organic chemicals had been obtained from Kahlbaum, and bulbs containing some 64 different liquids, rendered dust-free by repeated distillation *in vacuo*, were ready for a programme of quantitative studies of the *internal* light-scattering. This collection naturally proved very convenient also for the purpose of the comparative study of the surface-scattering, and the extended observations made possible by its aid served to bring out very clearly the influence on the phenomenon of the surface tension of the liquid, and thus to establish its *molecular* nature.

As already remarked in the first paper, in the case of transparent fluids, the surface-scattering is accompanied by the internal-scattering within the liquid when a pencil of light is concentrated upon the surface, but the two effects are distinguishable from each other in several particulars. By using a good achromatic lens to focus a well-defined image of the sun on the boundary, the surface opalescence appears as a sharply bounded circular or elliptic disc of light, whose aspect varies very much with the direction of observation while that of the internal-scattering does not. The colour of the surface opalescence is also much less blue than that of the internal-scattering, and, indeed, by contrast with it appears nearly white. Green, yellow and red filters held in front of the eye diminish the brightness of the volume effect much more (in increasing order) than they do that of the surface effect, and hence assist greatly

in studying or photographing the latter phenomenon. The brightness of the surface-scattering also varies with the direction of observation, while that of the internal-scattering in dust-free liquids is practically invariable. In the case of oblique incidence of the primary beam, the surface-opalescence is conspicuously brighter when viewed in directions adjacent to those of the reflected or transmitted pencils than in other directions. In fact, it then stands out very clearly, and may be distinguished even with liquids such as carbon disulphide or nitrobenzene, in which the internal-scattering is so strong that it usually overpowers the surface effect.

2. Comparative Study of the Surface-Scattering with Different Liquids.

The following is a list of the substances studied :—

Paraffins and Hydrocarbons.—Normal pentane, iso-pentane, hexane, heptane, octane, and iso-amylene.

Bromides.—Ethyl, propyl, iso-butyl, allyl and ethylene bromides.

Chlorides.—Normal propyl, iso-propyl, iso-butyl, allyl, methylene and ethylene chlorides, chloroform, carbon and silicon tetra-chlorides.

Sulphides.—Carbon disulphide, methyl and ethyl sulphides.

Fatty Acids.—Formic, acetic, propionic and butyric acids.

Oxides and Anhydrides.—Acetic and propionic anhydrides, ethyl-ether and water.

Benzene Derivatives.—Benzene, toluene, ethyl-benzene, ortho-, meta- and para-xylenes, benzyl and benzal chlorides, chlorobenzene, bromo-benzene, nitro-benzene, ortho-nitro-toluene and meta-nitro-toluene.

Alcohols.—Methyl, ethyl, normal propyl, iso-propyl, normal butyl and iso-butyl alcohols, trimethyl carbinol, amyl, allyl and benzyl alcohols.

Esters.—Methyl, ethyl and propyl formates, ethyl and propyl acetates.

Aldehyde and Ketones.—Acetaldehyde, di-methyl, methyl-ethyl, di-methyl and methyl-propyl ketones.

All these liquids show the phenomenon of surface-opalescence, but in varying degrees. In the entire list of substances studied, *water*, by reason of its high surface-tension and the ease with which it acquires a surface contamination, stands in a special position; the observations made on its surface-scattering will be described separately. The results obtained with the other liquids will now be summarized.

The lighter paraffins have a low surface-tension (15 to 20 dynes/cm.) and are found to show the surface-opalescence conspicuously. Not only is the effect intrinsically bright, but it is also seen well in contrast with the internal-scattering,

which is of very moderate intensity in these substances (about five times the internal-scattering in dust-free water). Ethyl bromide shows the effect moderately strongly. Some of the other bromides are liable to decomposition by the action of light and hence are not very suitable. The surface-scattering is found to be rather inconspicuous in ethylene bromide, which has a high surface tension (37 dynes/cm.), and also a large internal-scattering. All the chlorides studied show the surface-scattering conspicuously, carbon tetrachloride being specially strong. Carbon di-sulphide has an enormous internal-scattering (about 50 times that of pure water), and the surface-scattering can hardly be distinguished except for certain favourable directions of incidence and observation. Methyl and ethyl sulphides, on the other hand, show the effect quite strongly, their internal-scattering being relatively small.

The fatty acids afford a very interesting study. Formic acid has practically the same internal-scattering as acetic, propionic and butyric acids, but shows the surface-scattering much less conspicuously than those other acids. As the surface-tension of formic acid is notably higher than that of its three homologues, this furnishes a striking illustration of the relation between surface-tension and surface-opalescence. Ethyl-ether has a low surface-tension, about 15 dynes/cm., and the fact that it exhibits a strong surface-opalescence is another illustration of the general principle. The benzene derivatives all have a very strong internal-scattering, which tends to make their surface-opalescence somewhat inconspicuous. The alcohols (except benzyl alcohol) show the effect tolerably well, though not so strongly as ethyl-ether for instance. Acetaldehyde shows a conspicuous effect, while the esters show an effect of the same order of magnitude as the alcohols. The ketones are liable to decomposition, but such of them as can be obtained clear and dust-free (*e.g.*, acetone) show a conspicuous surface-scattering.

The comparative study of the effects shown by so many liquids, and the regularities and differences amongst them, afford the strongest possible demonstration of the molecular origin of the phenomenon and of its relation to surface-tension.

3. *Intensity and Polarisation of the Scattered Light.*

The intensity and the state of polarisation of the scattered light depends in a very interesting way upon the angle of incidence of the primary beam and the direction of observation. In order to save time and space, we shall give only a description of the phenomena noticed with a single liquid, ethyl-ether, which shows the surface-scattering strongly, and content ourselves with the

general remark that other liquids show very similar effects. It is possible, of course, that further quantitative and detailed studies may reveal features depending in a special way on the nature of the liquid and not merely on its physical constants, namely the surface-tension and refractive-index, which determine the general features of the phenomenon.

(a) *Light Incident Normally from Above.*—When unpolarised light is incident vertically on the horizontal surface of a liquid half-filling a spherical bulb, the surface-opalescence is barely visible from above, but is much more conspicuously seen from below the surface of the liquid. In the latter case, when viewed in a nearly vertical direction, the opalescent patch is quite distinct; as the eye is moved away to one side so as to view it more obliquely, there is no marked change in its intensity until the direction of observation is inclined to the vertical at an angle equal to the critical angle ($\sin^{-1} 1/\mu$) of the liquid, at which stage it suddenly brightens up. With further increase in the angle of observation there is a steady diminution in intensity until, for observation parallel to the liquid surface, the patch ceases to be visible.

The scattered light in nearly vertical directions is unpolarised. With the sudden increase in intensity which occurs at the critical angle, there appears also a remarkably complete polarisation of the scattered light with the electric vector parallel to the liquid surface. In more oblique directions this polarisation becomes partial.

(b) *Light Incident from Above at the Polarising Angle.*—When the primary beam, instead of falling normally, is incident obliquely on the liquid surface, the scattered light exhibits a notable asymmetry in its distribution of intensity, becoming much more marked in directions adjacent to the plane of incidence and lying between the transmitted and reflected rays than in others more remote. It continues, however, to be appreciably more distinct below than above the liquid surface. The light scattered *upwards* exhibits a polarisation which, for small angles of incidence, is partial, but becomes complete with the electric vector parallel to the surface, when the incidence is at the Brewsterian angle, practically for all angles of observation. The light scattered *downwards*, on the other hand, exhibits quite distinct phenomena; it shows little or no polarisation in the plane of incidence, but in a perpendicular plane shows strong polarisation with the electric vector *inclined* to the liquid surface and practically transverse to the track of the primary beam within the liquid.

(c) *Light Incident from Above nearly Grazing the Surface.*—In this case, again, it becomes somewhat difficult to see the opalescent area except from below the surface. The light scattered downwards into the liquid by the surface shows

polarisation effects very similar to those mentioned in the last sentence of (b) above.

(d) *Light Incident from Below nearly Grazing the Surface.*—In this case, of course, the beam of light is totally reflected. No surface-opalescence can be observed except in directions very close to that of total reflection ; it is then found to be completely unpolarised.

(e) *Light Incident from Below at the Critical Angle.*—The surface-opalescence is found to be much more conspicuous than in case (d), and can, in fact, be easily seen in all azimuths from below the surface, being most intense, however, in the plane of incidence and in directions adjacent to the reflected rays. From above it is not so distinct, and is best seen in directions nearly parallel to the liquid surface in the plane of incidence. The polarisation of the scattered light is most conspicuous in a plane at right angles to the plane of incidence, and when viewed nearly parallel to the liquid surface ; the principal component of the electric vector is then nearly vertical. In the plane of incidence, and in directions intermediate between the horizontal and the reflected rays, the scattered light is unpolarised. It is, however, partially polarised (with the electric vector horizontal) in directions intermediate between the vertical and the reflected rays.

(f) *Light Incident from Below at the Polarising Angle.*—As the angle of incidence is gradually altered from the critical to the Brewsterian angle for internal reflection, there is at first a remarkable increase, and then an equally remarkable diminution in the brightness of the opalescence as seen from above. At the polarising angle of incidence, the scattering is brightest seen from below ; the changes in its state of polarisation with the angle of observation are then extremely striking. Viewed in the plane of incidence from vertically below, it is strongly but not completely polarised ; as the direction of observation approaches that of the reflected rays, the intensity increases and at the same time the polarisation improves and becomes sensibly complete. On further increasing the angle of observation the scattered light brightens up rapidly further, but the polarisation becomes less perfect, and at the critical angle it nearly disappears. For directions of observation still more nearly horizontal, the scattered light is sensibly unpolarised. Viewed at right angles to the plane of incidence, the scattered light appears partially polarised, with the principal component of the electric vector inclined to the liquid surface, and practically perpendicular to the track of the primary beam within the liquid.

(g) *Light Incident from Below Normally.*—The phenomena noticed in this case are practically the same as for normal incidence from above.

Observations have also been made in the several cases noted above with the incident light *polarised* in or at right angles to the plane of incidence. A detailed description of them seems hardly necessary, as, except for directions of observation very remote from the plane of incidence, the character of the results is such as might reasonably be inferred from those noted above for the cases in which the incident light is unpolarised. The further consideration of the effect of polarising the incident light may, therefore, be deferred for the present.

4. *Measurement of the Intensity of the Surface-Opalescence.*

The scattering power of transparent liquid surfaces was compared with that of white plaster of Paris by the aid of suitable apertures and a revolving sector to reduce the illumination of the latter, in much the same way as was done in the case of metallic mercury. (Paper I.) In order to avoid errors due to the superposition of the internal-scattering, a case had to be chosen in which the surface-scattering was as intense as possible. For this purpose, the case in which the light was incident on the surface from below at the critical angle, was found to be the most suitable. The opalescence was most intense when viewed nearly in the direction of the reflected rays, and was brought into the field of view for comparison with the plaster of Paris with the help of a small silvered mirror suitably held. Two sets of measurements were made; the first was with methyl alcohol, to illustrate the manner in which the intensity of the opalescence varies with the azimuth of observation, the scattered light being always observed in a direction inclined to the vertical at nearly the critical angle (Table I). In the second set of measurements, the scattering powers of different liquids were determined in terms of plaster of Paris, to illustrate the order of magnitude of the effect and its dependence on the surface-tension and the refractive index of the fluid used (Table II).

Table I.—Methyl Alcohol, Intensity in various Azimuths.

Azimuth measured from plane of incidence.	0°	10°	20°	30°	40°	50°	60°	75°	90°
Intensity in terms of plaster of Paris $\times 10^6$	18.8	14.1	6.3	5.6	5.1	4.1	3.5	2.1	1.4

Table II.—Intensity measured with Red Light.

Substance.	Surface-tension in dynes/cm.	Refractive index.	Intensity as fraction of plaster of Paris.
Methyl alcohol	23	1.328	18.8×10^{-6}
Ethyl alcohol	22	1.360	21.3×10^{-6}
i-Propyl alcohol	21.3	1.376	21.3×10^{-6}
n-Butyl alcohol	24.4	1.400	25.8×10^{-6}
i-Butyl alcohol	22.8	1.395	33.4×10^{-6}
Tri-methyl-carbinol....	—	—	51.2×10^{-6}
Amyl alcohol	23.7	1.406	51.2×10^{-6}
Allyl alcohol	25.9	—	54.5×10^{-6}
Benzyl alcohol	—	1.536	38.0×10^{-6}
Ethyl-ether	15.3	1.352	43.4×10^{-6}
Pentane (normal)	15.0	1.359	39.3×10^{-6}

In Paper I the scattering power of mercury under approximately comparable conditions was given as 5.7×10^{-7} times that of plaster of Paris. The scattering power of methyl alcohol is thus about 33 times that of a metallic mercury surface. The surface-tension of mercury is some 547 dynes, and is thus about 23 times greater than that of methyl alcohol. Allowing for the fact that mercury reflects only about 70 per cent. of incident light, and taking into account its vastly higher surface-tension, its smaller surface-opalescence is readily understood. The greater the surface-tension, the more perfectly would the surface under thermal agitation approximate to a perfect optical plane, and the smaller would be the proportion of the incident light scattered by it in all directions.

5. Summary.

The paper describes observations and measurements made on the scattering of light by the surface of transparent liquids. Some 64 different substances were studied. The main results of the work may be stated as follows:—

(a) Surface-scattering is most conveniently observed with liquids that show a small internal-scattering; the lighter paraffins, ether, and the alcohols may be cited as examples.

(b) Other things being the same, a liquid having a higher surface-tension shows a smaller surface-opalescence and *vice versa*. Transparent liquids show an effect some 30 to 50 times more intense than that observed with metallic mercury.

(c) The variation of the intensity and state of polarisation of the scattered light with the angles of incidence and direction of observation shows some very remarkable features which are fully set out in the paper.

(d) Studies of the scattering of light by pure and contaminated surfaces of water, by liquid carbon dioxide at and near its critical temperature, and by the interfaces between different liquids under various conditions will be described in a further instalment of the work.

The Capture and Loss of Electrons by α -Particles.

By G. H. HENDERSON, Ph.D.

(Communicated by Prof. Sir E. Rutherford, F.R.S.—Received June 6, 1925.)

Introduction.

In a recent paper the writer* presented evidence of α -particles bearing a single positive charge and of α -particles which were neutral. These were found by deflecting α -particles by a magnetic field in a good vacuum and registering them photographically on Schumann plates. A band appeared on the plate deflected only half the amount of the regular α -particle band. This was ascribed to α -particles, which had captured electrons in passing through an absorbing screen and thus were singly-charged. The behaviour of these particles was described qualitatively. The proportion of singly- to doubly-charged particles increased rapidly as their velocity decreased. From the effects of air in the path of the α -particles it was suggested that each particle must capture and lose electrons many times.

Sir E. Rutherford† has recently published the results of a very interesting quantitative study of these particles by the scintillation method. By electrostatic deflection of the beam he showed that the particles undergoing only half the normal deflection must be singly-charged α -particles and nothing else. By counting methods he found values for the mean free paths for capture and for loss of an electron by the α -particle, and found the way in which these mean free paths varied with the velocity.

The mechanism involved in the capture and loss of electrons, particularly in the former, is difficult to understand. It is a matter of considerable interest to find out how these captures and losses occur in materials of widely different kinds, whose atoms contain different numbers of electrons with different degrees

* Henderson, 'Roy. Soc. Proc.,' A, vol. 102, p. 496 (1922).

† Rutherford, 'Phil. Mag.,' vol. 47, p. 277 (1924).

of binding to the nuclei. The main object of the present experiments was to investigate the ratio of singly- to doubly-charged particles in different materials and at various velocities.

While the counting of scintillations is the only possible quantitative method under certain circumstances, *e.g.*, at low velocities, yet it is very slow and tedious. For the work described in this paper the ionization method has been adopted and has proved satisfactory and relatively rapid. It is interesting to note that singly-charged particles have now been measured by three methods, *viz.*, photography, scintillations and ionization, with fairly concordant results.

Apparatus.

The apparatus used is shown in fig. 1. A is a brass box, $15 \times 8 \times 2$ cm., fitting between the pole pieces of a large electro-magnet, giving a field of 4,500

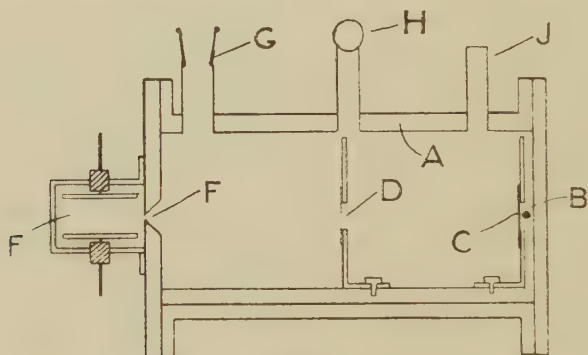


FIG. 1.

gauss. B is the wire source of radium active deposit, equivalent to from 1 to 6 mgm. radium. The platinum wire of 5 mm. diameter was previously activated when sealed into a glass tube into which radium emanation was pumped. The wire was made the cathode and the mercury confining the emanation the anode. Closely fitting around the glass wall of the tube and making contact with the mercury was a thin sheet of nickel, which made the potential gradient in the gas more uniform. By the use of this sheath as much as 60 per cent. of the active deposit could be concentrated on the wire with 220 volts.

Immediately in front of the source was placed the absorbing screen C. The α -rays passed through the 0.3 mm. slit D, and then out of the box through the 0.7 mm. slit E. The latter was covered with a collodion film which held a vacuum and had a stopping power for α -rays equivalent to about 4 mm. of air. These films were easily prepared by pouring a solution of collodion on a glass

plate. After the film dried it was cut by a knife into sections of suitable size, which were floated off on to water. They were then lifted on pieces of filter paper and allowed to dry on the paper. The films made in this way showed no signs of the frilling which often occurs when they are prepared on a mercury surface. The slit E was placed on the ground brass plate closing the end of the box. This plate could be slid up and down, moving the slit parallel to itself so as to pick out any part of the "spread out" beam of α -particles. Its position could be read on a scale fixed to the box.

The ionization chamber F was also attached to this movable plate. It consisted of a closed cylinder within which were two parallel plates, one of which was kept at a potential of 100 volts and the other connected to a Compton electrometer (sensitivity 2,000 mm. per volt approx.). A thin aluminium plate could be moved by means of the ground joint G so as to cut off the beam of α -rays. Since the ionization current due to the α -particles was very small, the current due to β - and γ -rays was reduced by balancing against it the β - and γ -ray ionization from the nickel sheath used in activating the source. This auxiliary source, which decayed with the same period as the wire, was placed so as to ionize the air in one of the brass tubes shielding the wire leading to the electrometer. The brass tube was raised to a suitable potential, and the position of the auxiliary source adjusted at the beginning of the experiment so as to reduce the movement of the electrometer needle almost to zero in the absence of α -rays. This residual ionization current remained small, changing only very slightly in several hours. It was frequently measured and allowed for in the course of an experiment.

The tube H led to a discharge tube by which the nature of the vacuum was usually judged. The tube J led to a liquid-air trap for mercury and other vapours, and thence to the pump system, consisting of two Volmer-type mercury diffusion pumps backed by an oil pump. Under working conditions practically no discharge could be seen in the tube. Tested by a McLeod gauge the pressure was less than two or three ten-thousandths of a millimetre the limit of the gauge. This was amply sufficient to avoid any disturbing effects of gas on the α -particles. Most of the experiments were carried out with liquid air surrounding the trap. However, it was found that with the trap at about -10° C., or even room temperature, no disturbing effect of mercury vapour was noticed. This, of course, refers to α -particles of the fairly high velocities dealt with in this paper.

Experiments.

The α -particles were studied at velocities ranging from $1.0 V_0$ to $0.4 V_0$, where V_0 is the velocity of the α -particles from RaC (1.922×10^9 cm. per sec.). The lower limit was set by the collodion window. No attempt was made to detect neutral particles, which are rare even at the lower limit of the velocities dealt with.

The primary object of these experiments was to determine whether the fraction of the α -particles which were singly-charged depended on the material through which the particles passed. Accordingly most of the absorbing screens used were either gold or mica, two substances which provided the most uniform thickness of foil and presented a wide difference in atomic number of their constituent atoms. Composite screens of suitable stopping-power were made, consisting of a sheet of mica on one side of which were pressed six or eight thicknesses of gold foil (total 3 or 4 mm. air equivalent). This screen was placed with its mica face towards the ionization chamber and an experiment carried out. The screen was then reversed with its gold face towards the ionization chamber and the experiment repeated. The relative effects of gold and mica were thus compared at almost identical velocities. The charged condition of a particle on emerging from the screen depended only on the material comprising the last few millimetres (air equivalent) of the foil, for it frequently gained or lost an electron, and thus quickly established an equilibrium in a new material. The α -particle, so to speak, soon forgets its previous history.

This property also proved useful in measuring the ionization due to the different particles. The beam of singly-charged particles must have been changed in passing through the collodion window into a mixture of singly- and doubly-charged particles in equilibrium, and the same thing must have been true of the doubly-charged beam. Thus, no matter how different the ionizing powers of the two kinds of particles, the current in the ionization chamber was proportional to the number of α -particles passing through the window, regardless of their nature.

The procedure of an experiment was as follows:—The radioactive source was prepared and measured, then inserted in the apparatus about 20 minutes after removal from the emanation. The pumps were started, the magnetic field applied and the γ -ray ionization balanced out as described above. The end-plate was moved so that the slit came about the middle of the singly-charged beam. Measurements commenced from 40 minutes to 1 hour after removal of the source from the emanation. The slit was set at different parts of the singly-charged beam and the corresponding ionizations were measured.

Then the magnetic field was reduced to exactly half strength and the doubly-charged beam was measured in the same manner. It was found essential to measure the doubly-charged beam at half field, partly so as to ensure identical geometrical conditions, but mainly on account of the inhomogeneity of the beam. The widths of the two beams so measured were about equal, but the doubly-charged beam measured with full field was much wider, and the maximum intensity less, than at half field. This decrease in intensity was, of course, more marked at low velocities. For instance, at about 0.4 V the maximum at full field was only about 50 per cent. of the same maximum at half field.

The ionization currents were corrected for decay by means of Hess and Lawson's* tables. It is possible that the decay of the active deposit in the first hour may depend somewhat on the geometrical arrangement of the source being activated, but after the first hour the decay takes place with practically the period of radium B, and will in all probability be the same in all cases.

Results.

The results of two typical experiments are shown in fig. 2. The abscissæ represent the position of the slit, measured from an arbitrary zero, and the ordinates the corrected rates of electrometer deflection on two different scales in divisions per second. Doubly-charged α -particles are designated He_{++} and singly-charged He_{+} ; the ratio of the numbers of doubly- and singly-charged particles may be written $\text{He}_{++}/\text{He}_{+}$. In fig. 2, $\text{He}_{++}/\text{He}_{+}$ for gold = 25.7, and for mica = 26. The velocity corresponding to the maximum of the beam in both cases is 0.56 V_0 .

The results of a number of such experiments are shown in Table I, which gives values of $\text{He}_{++}/\text{He}_{+}$ and the corresponding velocities for α -particles emerging from mica, gold, copper, aluminium and silver, as well as from a bare source. These results are plotted in fig. 3. To show results on a reasonable scale, values of the one-third power of $\text{He}_{++}/\text{He}_{+}$ are plotted against the velocity. The results of Rutherford are also included.

The accuracy in these results is not high. The ionization currents are usually small and hard to measure. There is also the difficulty of estimating the maximum of the curves. The errors are greatest for both very high and very low velocities; in the one case because of the small fraction of He_{+} , in the other because of the small intensity of the beam. For intermediate velocities the

* Hess and Lawson, 'Wien. Ber.,' vol. 127.

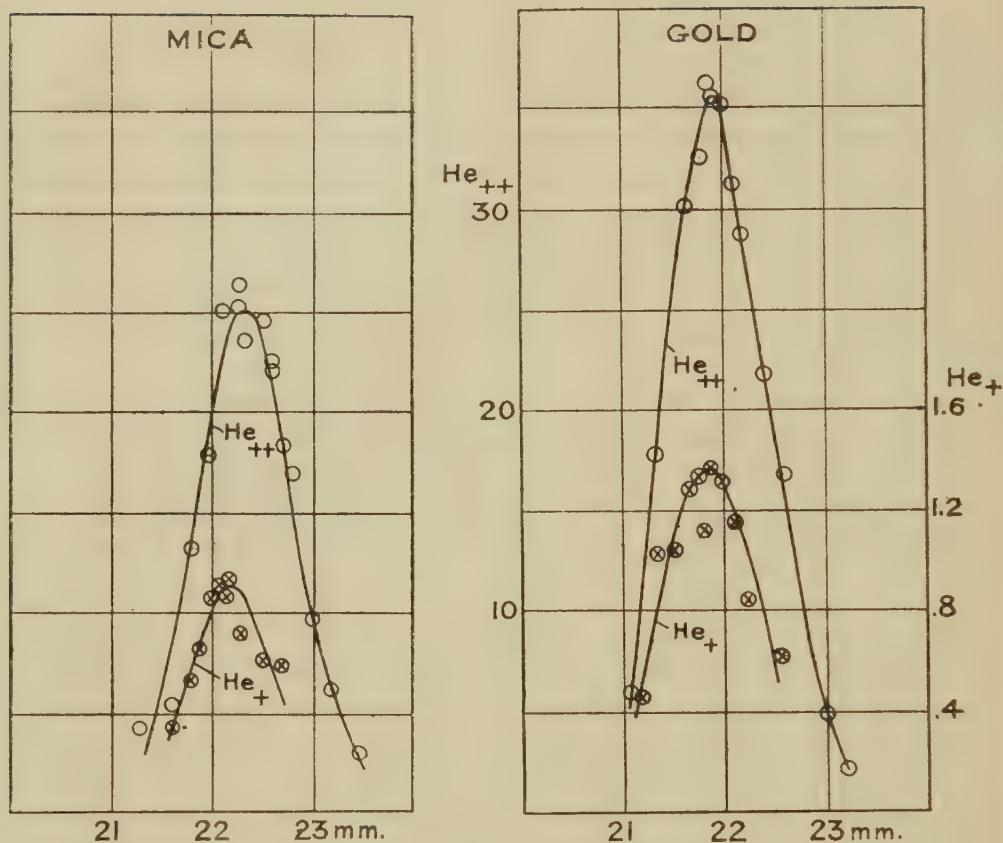


FIG. 2.

Table I.

α -particles emerging from	Velocity. $V_0 = \text{unity.}$	$\text{He}_{++}/\text{He}_{+}$.
Bare Pt wire	1.00	161.0
Mica	0.88 ₆	126.0
Gold	0.88 ₆	113.0
Mica	0.80	82.2
Copper	0.74 ₅	66.6
Gold	0.66 ₆	41.6
Gold	0.59 ₅	27.1
Mica	0.59 ₅	29.8
Gold	0.56 ₀	23.1
Mica	0.56 ₀	24.7
Mica	0.56 ₀	26.0
Gold	0.56 ₀	25.7
Aluminium	0.55 ₀	21.4
Mica	0.50 ₂	15.4
Gold	0.50 ₂	14.3
Silver	0.44 ₅	7.65
Mica	0.42	6.27
Gold	0.40 ₅	6.3
Mica	0.40 ₅	5.4

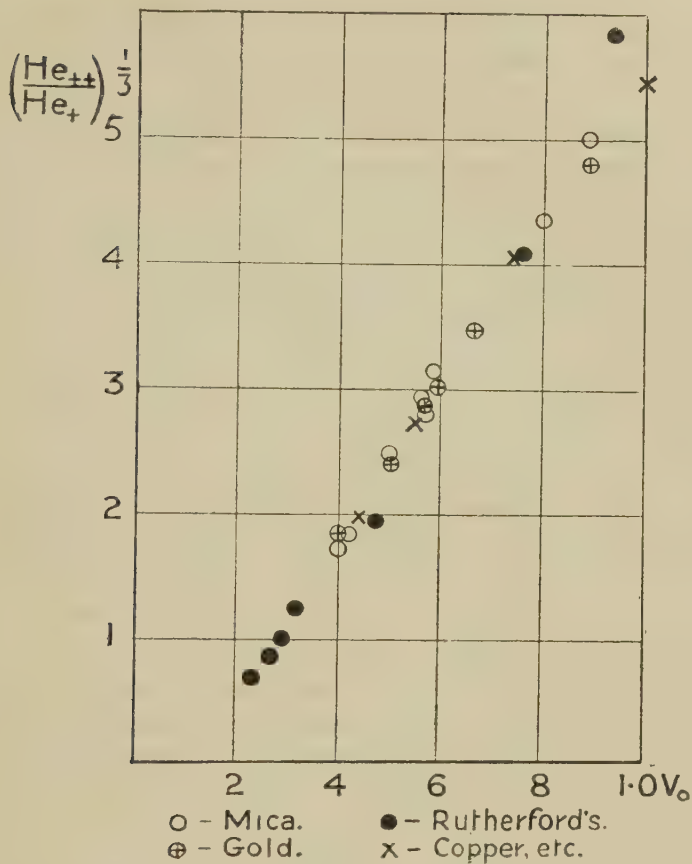


FIG. 3.

probable error may amount to 5 per cent., which may possibly be doubled at the extreme ends of the velocity scale.

Discussion.

From the results of Table I and fig. 3, it seems clear that the ratio of doubly-charged to singly-charged particles in equilibrium at any velocity is independent of the material through which the α -particles are passing. This seems to hold true within the limits of error for all the materials tested, over the whole range of velocity covered, viz., from V_0 to $0.4 V_0$. Values of $\text{He}_{++}/\text{He}_{+}$ for rays emerging from gold, mica, aluminium, silver and copper all lie on the same curve within the limits of error.

From theoretical considerations Fowler* had predicted that $\text{He}_{++}/\text{He}_{+}$ for

* Fowler, 'Phil. Mag.,' vol. 47, p. 416, February, 1924.

gold should be about 2.4 times that for mica. It can readily be seen that such a difference should easily be detected in these experiments if it existed. It is convenient to use the concepts of a mean free path for capture λ_1 , and a mean free path for loss of an electron λ_2 . Rutherford has shown that $\lambda_1/\lambda_2 = \text{He}_{++}/\text{He}_+$. He has also found experimentally that λ_2 depends upon the material through which the particle is passing, being 4 to 5 times longer in hydrogen and 5 to 6 times longer in helium than in air. Thus λ_2 varies approximately inversely as the ionization per unit path produced by the α -particles in these gases. Rutherford has also found that λ_2 is approximately proportional to the velocity of the α -particle. The behaviour of λ_2 with respect both to material and to velocity is what might be expected in view of the correspondence of loss of an electron to ionization.

From the present results it appears that λ_1/λ_2 is independent of the material. We must therefore conclude that λ_1 varies inversely as the ionization per unit path, produced by the α -particle in the material. On the other hand, anticipating the subsequent discussion of the point, λ_1 varies as the third and higher powers of the velocity. We are thus confronted with the situation that whereas λ_1 and λ_2 vary in a similar manner with the material traversed, yet they show marked differences in their variation with velocity.

This might be explained in the following way. Before capture can take place the atoms of the material must be ionized. It would seem reasonable to suppose that the greater the number of electrons set free in a definite length of the path of a He_{++} particle, the greater would be the probability of capture of an electron. Thus we might expect λ_1 to vary inversely as the ionization per unit path, and hence that λ_1/λ_2 or $\text{He}_{++}/\text{He}_+$ should be independent of the material. On the other hand, without discussing the mechanism of capture, in which possibly the aid of a third body must be invoked, we should expect that the chance of capture would depend to a very marked degree upon the velocity of the particle. It is not surprising therefore that λ_1 should change rapidly with the velocity and in this respect differ very much from λ_2 .

What follows is a short discussion of the variation of λ_1/λ_2 with velocity. Rutherford expressed his results on the assumption that λ_1/λ_2 varied as V^n and found the average value of $n = 4.6$. On testing the present results on the same assumption it was found that n was not constant, but increased as the velocity decreased. The results were treated in the following way:—The nineteen experimental values of $\lambda_1/\lambda_2 (= \text{He}_{++}/\text{He}_+)$ in Table I were arranged in order of decreasing velocity. Taking together the 1st and 10th, 2nd and 11th, etc., values of n were found. The first five of these ten values

of n so found gave a mean value of $n = 3.4$, with a mean error without regard to sign of 0.15 . The average velocity of the α -particles in this group was $0.70_4 V_0$. For the last group of five values of n the mean was 4.3 ± 0.3 , and the average velocity $0.51_5 V_0$.

The change in n is much too great to be ascribed to experimental error. Furthermore, since this change seems real, part of the mean of the errors, which were averaged without regard to sign, must be due to this change, and the values of n may be more accurate than indicated above.

If the last four of the values in Table I be combined with the last four given by Rutherford the value of n is found to be $4.9 \pm 0.3_5$ at an average velocity of $0.3_5 V_0$, in agreement with the trend of n given above. Of the remaining three values of $\text{He}_{++}/\text{He}_+$ given by Rutherford, one agrees with the present results, while two differ considerably, as can be seen from fig. 3.

Thus, assuming that λ_1/λ_2 varies as V^n , there seems to be a regular increase of n as the velocity diminishes. This variation is given approximately by the equation :—

$$n = 6.4 - 4.2 V/V_0.$$

This expression is, of course, to be taken only as a rough expression of the values observed within the range of velocity covered. In view of the experimental errors it does not appear profitable to find a better mathematical relationship between the observed values of λ_1/λ_2 and V .

Summary.

α -particles with a single positive charge have been detected by their ionization, and the ratio of the number of doubly-charged to the number of singly-charged α -particles in equilibrium has been found quantitatively under various conditions. It has been found that this ratio is independent of the material through which the particles moved. The variation of this ratio with the velocity of the α -particles has been determined.

These experiments were carried out in the University of Saskatchewan, Saskatoon, Canada. I wish to express my gratitude to the President and the members of the Physics Department of that institution for their very cordial and generous assistance.

β -Ray Spectra of Thorium Disintegration Products.

By D. H. BLACK, M.Sc., Emmanuel College, Cambridge.

(Communicated by Prof. Sir E. Rutherford, F.R.S.—Received June 6, 1925.)

In problems relating to atomic structure the study of β -ray spectra is becoming of increasing importance. It is therefore desirable that an accurate analysis should be made for as many substances as possible which emit β rays. This has been done in great detail by Ellis,* and by Ellis and Skinner,† for radium B and radium C, and they have shown that the γ rays which eject the electrons from the atoms can be arranged in a system of levels. Recently the author made an analysis of the β -ray spectrum of mesothorium 2,‡ and found that most of the γ rays from this substance could also be accounted for by a system of levels.

The β -ray spectrum of thorium B and of thorium C + D had previously been measured by Ellis§ and also by Meitner.|| Since that time the technique of the measurement of β -ray spectra has been greatly improved. Therefore, considering the importance of such measurements in modern atomic theories, it was most essential that an accurate analysis of the spectrum of these substances should be made. Moreover, the previous measurements for these spectra were based on the then accepted values for lines of the radium B spectrum, which recent work has shown to need a small correction.

No attempt was made to find all the lines measured by Ellis, for it was only necessary to obtain values for the principal lines, the fainter ones being obtained by interpolation. Nevertheless, several new lines have been recorded, one group in particular being of great interest on account of their high energy, which exceeds 2·5 million volts.

Experimental Results.

The analysis was performed by separating the β rays into a spectrum by a magnetic field, using the focussing method. The apparatus was the same as was used in the determination of the spectrum of mesothorium 2. The strength of the magnetic field, H , was obtained in the same manner as previously

* ‘Roy. Soc. Proc.,’ A, vol. 99, p. 261 (1921), and vol. 101, p. 1 (1922).

† ‘Roy. Soc. Proc.,’ A, vol. 105, p. 165 (1924).

‡ ‘Roy. Soc. Proc.,’ A, vol. 106, p. 632 (1924).

§ ‘Proc. Camb. Phil. Soc.,’ vol. 21, p. 121 (1922), and ‘P. R. S.,’ vol. 101.

|| ‘Zeit. f. Phys.,’ vol. 9, p. 131 (1922).

described, namely, by calculating from the standard values of H_0 for radium B. The measurements are taken from 17 plates, using nine different values for the magnetic field. The maximum error is 1 in 250, and in most cases is less than this.

The sources used were thorium B, with thorium C and thorium D in equilibrium. These were prepared in the following manner: A solution of radiothorium was made slightly acid with nitric acid and then electrolysed, using platinum electrodes. The thorium B was deposited on the anode, a platinum wire 0.25 mm. in diameter. The electrolysis usually lasted for at least sixteen hours, so that the thorium C and thorium D would be in equilibrium with the thorium B. Sources having an activity of as much as 8 mgm. of radium have been obtained in this way.

As has been mentioned, no attempt was made to obtain all the lines of the spectra concerned, and therefore comparatively short exposures were made except in one or two cases. It was to be expected, then, that Ellis's analysis would give many lines which did not appear in the present one, and this was found to be the case.

Nevertheless, a number of lines have been recorded which were not mentioned by Ellis. In his analysis he used separate sources of thorium C + D as well as sources of thorium B. The sources of thorium B which were then obtainable were very weak and only small value exposures were possible. On the other hand, he made relatively long exposures with thorium C + D.

In the present work the exposures were practically the same for all the products. Therefore it is natural to assume that any lines which appear in this analysis, but which are not recorded by Ellis as being due to thorium C + D, are due to β rays from thorium B. There are, however, two groups of lines which are not to be attributed to this substance. They are the above-mentioned high-energy lines which are attributed to thorium D, and a group of lines which are almost certainly due to radium D.

The spectra of each of the products will be given separately, together with the classification of most of the lines into groups corresponding to the ejection of electrons from the various absorption levels by γ rays. It will be noticed that two classifications are made, in each case with absorption levels corresponding to the two atomic numbers of the atoms concerned, before and after the nuclear change has taken place. The reasons for this will appear later.

The energies of the absorption levels concerned are tabulated below. Their values are taken from the results of Bohr and Coster.*

* 'Zeit. f. Phys.,' vol. 12, p. 350 (1923).

Table I.—Absorption Energies.

Level.	Atomic No. 81.	Atomic No. 82.	Atomic No. 83.
K	0.852×10^6 volts	0.875×10^6 volts	0.900×10^6 volts
L _I	0.153	0.158	0.164
L _{II}	0.147	0.152	0.157
L _{III}	0.126	0.130	0.134
M _I	0.037	0.038	0.040
M _{II}	0.034	0.035	0.037
M _{III}	0.030	0.031	0.032
M _{IV}	0.025	0.026	0.027
M _V	0.024	0.025	0.026
N	0.009–0.001	0.009–0.001	0.010–0.002

Thorium B.

The general appearance of the spectrum of thorium B is shown in the accompanying diagram.



It is not possible to give a correct idea of the relative intensity of the very strong line of H γ 1398. Tables II and III give the values of the lines and their classification into the groups corresponding to the conversion of γ rays. The intensities of the lines are approximate only and are on a similar basis to that used for the β -ray spectrum of mesothorium 2.*

It is also possible to assume that the first group of lines in Table III are due to the conversion of the ordinary K X-radiation of thorium B. The agreement of the calculated with the measured energies is shown in the accompanying table, and this is in all probability the correct explanation.

This leaves six lines unclassified. Of these it is possible that line number 8 of energy 1.419×10 volts, which is comparatively strong, may be due to the conversion of a γ -ray in the K level. The corresponding line for the same ray acting on an L level would have an energy of 2.117×10 volts, which would be too close to the strong line number 11 to be distinguished from it. Although these lines have been attributed to thorium B it is quite possible that they might be due to radium D, but the former seems the more likely case.

* D. H. Black, *loc. cit.*

Table II.—Thorium B Spectrum.

No.	Intensity.	H ρ .	Energy (volts $\times 10^{-5}$)
1	10	835	0.583
2	4	856	0.611
3	2	926	0.709
4	2	946	0.738
5	4	1020	0.849
6	20	1118	1.006
7	1	1185	1.119
8	30	1352	1.419
9	200	1398	1.506
10	4	1452	1.610
11	30	1701	2.118
12	80	1764	2.254
13	30	1820	2.376
14	6	1831	2.399
15	1	1926	2.605
16	3	2037	2.854
17	1	2095	2.998

Table III.

No.	Intensity.	Energy.	Atomic No. 82.		Atomic No. 83.	
			Level of Origin.	Energy of γ -ray.	Level of Origin.	Energy of γ -ray.
1	10	0.583×10^5 volts.	L _I	0.741×10^5 volts.	L _I	0.747×10^5 volts.
2	4	0.611	L _{III}	0.741	L _{III}	0.745
3	2	0.709	M _{III}	0.740	M _I	0.749
4	2	0.738	N _{VI}	0.741	N _I	0.748
9	200	1.506	K	2.381	K	2.406
12	80	2.254	L _{III}	2.384	L _I	2.418
13	30	2.376	M _V	2.401	M _I	2.416
14	6	2.399	—	—	N	2.409
11	30	2.118	K	2.993	K	3.018
16	3	2.854	L _{III}	2.984	L _I	3.017
17	1	2.998	—	—	M _I	3.038

Table IV.

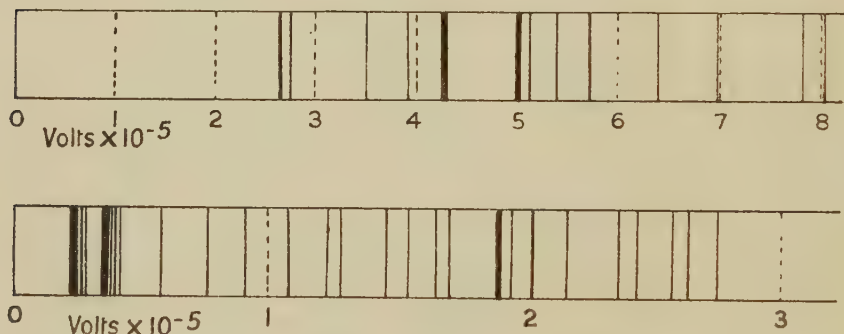
No.	Intensity.	Energy of line.	Atomic No. 82.		Atomic No. 83.	
		(volts $\times 10^{-5}$).	Origin.	Energy calc.	Origin.	Energy calc.
1	10	0.583	K α_1 — L _I	0.587	K α_2 — L _I	0.579
2	4	0.611	K α_1 — L _{III}	0.615	K α_2 — L _{III}	0.609
3	2	0.709	K α_1 — M _I	0.707	K α_2 — M _{III}	0.711
4	2	0.738	K α_1 — N	0.738	K α_2 — N	0.738

Thorium C + D.

As pointed out by Ellis,* it is very difficult to decide whether the β rays are emitted by thorium C or by thorium D, but he considers that in all probability the lines are almost entirely due to thorium D. Thorium C emits γ rays in small quantities only, and the greater part of the γ -ray radiation from thorium C + D is to be ascribed to thorium D. This would suggest that the β -ray lines, being due to conversion of γ rays, come from thorium D.

The numerical agreement obtained by assuming that the β rays are due to the conversion of γ rays in atoms of either thorium C or thorium D, also strongly suggests that the greater number, at any rate, of the β -ray lines have their origin in thorium D. For these reasons the lines are classified as coming from atoms whose atomic number is either 81 or 82, corresponding to the similar two cases for thorium B.

The general appearance of the spectrum is shown in the following diagram.



In addition to the lines shown there is also the group of very high energy. These are assigned to thorium D because it is known that neither thorium B nor thorium C have a very penetrating γ -ray radiation, while thorium D has.

Of the forty lines given in the following table, sixteen have been measured in the present analysis, and the remaining ones derived from Ellis's values by interpolation. The lines having the intensity indicated by a number as well as by letters are those recorded in the present work. Of these lines twenty-eight can be accounted for by assuming γ rays as shown in the succeeding tables. The remaining lines may be due to conversion of γ rays in the K level with the corresponding L lines too faint to be seen; but they are not tabulated as such.

* *Loc. cit.*

Table V.—Thorium C + D Spectrum.

No.	Intensity.	H ρ .	Energy (volts $\times 10^{-5}$).
1	v.s. 100	541	0.252
2	s. 6	548	0.259
3	m.	568	0.278
4	v.s. 60	658	0.369
5	m.	668	0.380
6	s. 25	684	0.398
7	m.	689	0.404
8	f.	830	0.577
9	f.	960	0.758
10	f.	1,056	0.906
11	m.	1,157	1.071
12	m.s.	1,249	1.231
13	f.	1,278	1.283
14	m.s.	1,373	1.458
15	f.	1,421	1.550
16	m.s. 2	1,478	1.661
17	m.	1,501	1.706
18	v.s. 30	1,604	1.915
19	m.f.	1,623	1.954
20	s. 4	1,665	2.042
21	m.f.	1,723	2.165
22	f.	1,817	2.369
23	m.	1,852	2.446
24	m.f.	1,916	2.583
25	m.s. 3	1,939	2.640
26	m.s. 2	1,990	2.756
27	f.	2,312	3.515
28	f.	2,475	3.913
29	v.s. 12	2,622	4.281
30	v.s. 10	2,913	5.025
31	m.f.	2,961	5.150
32	m.f.	3,057	5.400
33	m.s. 2	3,182	5.729
34	m.s. 1	3,432	6.397
35	m.f.	3,650	6.990
36	m.s.	3,960	7.836
37	f.	4,040	8.057
38	4	10,080	25.58
39	1	10,340	26.35
40	0.5	10,380	26.46

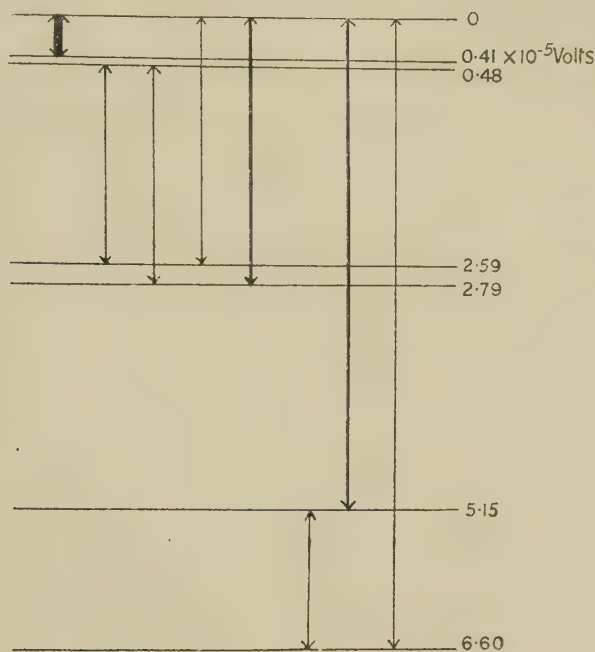
Table VI.

—	Intensity.	Energy of Line (volts $\times 10^{-5}$).	Atomic No. 81.		Atomic No. 82.	
			Level of origin.	Energy of γ -ray.	Level of origin.	Energy of γ -ray.
1	V.S. 100	0.252	L _I	0.405	L _I	0.410
2	S. 6	0.259	L _{II}	0.406	L _{II}	0.411
3	M. 6	0.278	L _{III}	0.404	L _{III}	0.408
4	V.S. 60	0.369	M _I	0.406	M _I	0.407
5	M. 6	0.380	M _V	0.405	M _V	0.406
6	S. 25	0.398	N _I	0.407	N _I	0.407
8	F. 6	0.577	K	1.429	K	1.452
13	F. 6	1.283	L _I	1.436	L _I	1.441
12	M.S. 6	1.231	K	2.083	K	2.103
19	F. 6	1.954	L _{III}	2.080	L _I	2.112
14	M.S. 6	1.458	K	2.310	K	2.333
21	M.F. 6	2.165	L _{III}	2.291	L _I	2.323
16	M.S. 2	1.661	K	2.513	K	2.536
22	F. 2	2.369	L _{III}	2.522	L _I	2.527
17	M. 2	1.706	K	2.558	K	2.581
23	M. 2	2.446	L _{III}	2.572	L _I	2.604
18	V.S. 30	1.915	K	2.767	K	2.790
25	M.S. 3	2.640	L _{III}	2.766	L _I	2.798
20	S. 4	2.042	K	2.894	K	2.917
26	M.S. 2	2.756	L _{III}	2.882	L _I	2.914
29	V.S. 12	4.281	K	5.133	K	5.156
30	V.S. 10	5.025	L _{III}	5.151	L _I	5.183
31	M.F. 10	5.150	—	—	M _I	5.188
33	M.S. 2	5.729	K	6.581	K	6.604
34	M.S. 1	6.397	L _{III}	6.523	L _I	6.555
38	4	25.58	K	26.43	K	26.46
39	1	26.35	L _{III}	26.48	L _I	26.51
40	0.5	26.46	M	26.49	M	26.49

Table VII.—Energies of γ Rays of Thorium D (in volts $\times 10^{-5}$).

Atomic No. 81.	No. of γ -ray.	Atomic No. 82.
0.405	1	0.408
1.432	2	1.446
2.082	3	2.108
2.300	4	2.328
2.518	5	2.532
2.565	6	2.592
2.766	7	2.794
2.888	8	2.916
5.142	9	5.176
6.552	10	6.580
26.470	11	26.490

An attempt has been made to account for the eleven γ rays as being due to a system of nuclear levels. The problem does not appear to be so simple as in other cases, but a diagram is given which accounts for eight of the γ rays fairly successfully. Comparison with Ellis's suggested classification shows that they agree to a large extent; and also that it is similar to the systems derived for radium B and radium C.



Radium D.

It was noticed that on some of the plates covering the lower part of the region investigated, one or two lines appeared very strongly, while on others they were not visible. Also some lines appeared strongly on some plates and weakly on others. On calculating the energies of these particular lines a group of four was found whose energies agreed with the energies for radium D, which had been measured by Danysz* and by Ellis.† The latter records five lines, four of which appear here, these being the same as the four recorded by Danysz.

The presence of radium D on the sources is easily explained by the fact that radium was present in the original solution, being an isotope of mesothorium 1. Radium D would be electrolysed out with the thorium products,

* 'Le Radium,' p. 1 (Jan., 1913).

† 'Camb. Phil. Proc.,' vol. 21, p. 125 (1922).

and if a second source were prepared soon after the previous one, the amount of radium D present on it would be smaller in comparison with the amount of thorium B in the two cases. It was also found that, on testing the sources after an interval of some considerable time, traces of polonium were present, thus proving beyond doubt that radium D was present on some of the sources.

The following tables give the values of the lines and their levels of origin: the four lines being accounted for by the conversion of one γ -ray. The previously accepted values of $H\rho$ are also given, and it will be noticed that these are slightly higher than in the present case. The difference corresponds to the difference between the previously accepted and now known values of the radium B lines with which they were compared in each case.

Table VIII.—Radium D Spectrum.

No.	Intensity.	Previously accepted $H\rho$.	$H\rho$ observed.	Energy (volts $\times 10^{-5}$).
1	50	600	600	0.309
2	2	605	606	0.315
3	20	717	714	0.433
4	10	742	738	0.461

Table IX.

No.	Intensity.	Energy (volts $\times 10^{-5}$).	Atomic No. 82.		Atomic No. 83.	
			Level of origin.	Energy of γ -ray.	Level of origin.	Energy of γ -ray.
1	50	0.309	L_I	0.467	L_I	0.473
2	2	0.315	L_{II}	0.467	L_{II}	0.472
3	20	0.433	M_{II}	0.468	M_I	0.473
4	10	0.461	N_{III}	0.467	N_I	0.471

Discussion.

The results of this investigation give further strong support to the now generally accepted hypothesis that the lines of β -ray spectra are due to the conversion of γ rays in the various absorption levels of the atoms concerned. One of the outstanding problems in the interpretation of these spectra is to determine whether the γ -ray is converted before or after the nuclear change takes place. This matter has already been discussed in dealing with the β -ray spectrum of mesothorium 2; and, as in that case, the tables given in this analysis show possible classifications of the β rays for the two atomic numbers concerned.

In discussing the results for mesothorium 2, I came to the conclusion that there was some slight evidence in favour of the view that the conversion of the γ -ray takes place after the nuclear change. The same argument would appear to hold in the present case, namely, that one would not expect to find sudden changes in the relative intensities of β rays emitted from the L_I and L_{II} levels as the energy of the ray increased. (In dealing with mesothorium 2 the L_{II} level was considered, instead of the L_I level as here, but the argument still holds.)

Slight further evidence in support of this contention is found from an examination of the classification of the β rays from thorium B (Table III). It will be noticed that in the case of the group for which the very strong line represents the conversion of the γ -ray in the K level, it is possible to include a line due to conversion in an N level, if the atomic number is 83, but not if it is 82. A similar case seems to occur in the succeeding group, an M level being the one in question. Naturally, too much weight cannot be placed on such an important problem from such slight evidence; but such as it is the evidence does seem to point to the fact that electrons are ejected from the various levels after the nuclear change has taken place.

As has already been mentioned, a point of great interest was the detection of a group of lines of high energy. These lines are thought to be due to thorium D, for the reasons already given, but one cannot be certain of this point. Despite their high energy, these lines are almost certainly due to the conversion of a single γ -ray in the K and L levels of an atom, and also possibly in an M level. Ellis* has recorded two lines in the spectrum of radium C which are due to the conversion in the K and L levels of a ray of energy 2.22 million volts. The fact that the energy of the highest γ -ray recorded from thorium D is greater than the corresponding ray from radium C by nearly half a million volts explains why, in absorption experiments, γ rays from thorium D have a lower absorption coefficient than those from radium C.

In comparing these high energy lines with those from radium C it is also interesting to note that, while in the case of radium C there are a number of well marked groups of lines whose energies lie between one and two million volts, in the case of thorium D there appear to be no lines at all within this region except those mentioned above. If there are any lines present within this region they are exceedingly faint, as an exposure of as much as 40 mgm. hours was made on one occasion. While no lines appear to be present, yet there does appear to be a continuous background. It should be noted, however,

* 'Proc. Camb. Phil. Soc.,' vol. 22, p. 369 (1924).

that this continuous background does not extend as far as the group of high energy lines, but disappears at about 2·2 millions volts.

In connection with this group of high-energy lines it is interesting to note that Yovanovitch and d'Espine* record a line of energy 2·6 million volts from mesothorium 2. It is not possible that the lines recorded above come from that substance, as no trace of the stronger lines of the mesothorium 2 spectrum appeared on any of the plates.

In conclusion, I have to thank Sir Ernest Rutherford for his continued interest and advice during the course of the work. I have also to thank Dr. C. D. Ellis for very kindly making an exposure of the high energy region on his apparatus, which has a greater resolving power than the one I have used; and also for much helpful advice and criticism. My thanks are also due to Dr. J. Chadwick for so kindly preparing the thorium B sources; and to Mr. G. R. Crowe for preparing the radium B + C sources used.

The Flame Spectra of Carbon Monoxide and Water-Gas.—Part I.

By FRANK R. WESTON, B.Sc., D.I.C.

(Communicated by Prof. W. A. Bone, F.R.S.—Received 11 June, 1925.)

[PLATES 1 and 2.]

As part of my work as the Gas Light & Coke Company's Research Fellow in the Department of Chemical Technology at the Imperial College of Science and Technology, South Kensington, I was asked to undertake a systematic investigation of the flame spectra of carbon monoxide, and of mixtures of carbon monoxide and hydrogen, under the joint supervision of Prof. W. A. Bone and Prof. A. Fowler, with a view to the elucidation, if possible, of certain aspects of the combustion of carbon monoxide which have been referred to in recent publications upon the subject. The present paper embodies the results of my experiments.

The characteristic blue appearance of the highly radiative flame of carbon monoxide burning in air is, of course, well known; but on looking into the literature of the subject, very little appears to have been published concerning

* 'Compt. Rend.,' vol. 179, p. 1,162 (1925).

the flame spectrum of carbon monoxide, which has not yet been adequately described. In 1901 Smithells* recorded that the flame of carbon monoxide gives a continuous spectrum whether burning in air, oxygen or nitrous oxide, and that the same is also true when the combustion is inverted by burning oxygen in an atmosphere of carbon monoxide. He referred also to a previous observation of Burch's† that when the gas is burnt under reduced pressure, its spectrum becomes discontinuous, and that the maxima of light, though ill-defined, are in such positions as suggest that they are vestiges of oxy-carbon bands.

More recently, Barratt,‡ in discussing the origin of the banded flame spectrum of cyanogen burning in air, stated that the so-called continuous spectrum of a carbon monoxide flame is distinctly banded, and the between wave-lengths 5000 and 3000 Å.U. it is crossed by many bands at an average interval of about 20 Å.U. apart. The investigations described herein have confirmed and extended these observations, and have also shown that the gradual admixture of hydrogen with burning carbon monoxide has a profound influence upon the flame spectrum, which is of significance in connection with the mechanism of the combustion.

From the chemical point of view, we are as yet far from understanding the mode of combustion of carbon monoxide. Ever since H. B. Dixon's discoveries that a perfectly dry mixture of carbon monoxide and oxygen in combining proportions does not explode when electric sparks of ordinary intensity are passed through it, and that a flame of dry carbon monoxide is easily extinguished on being introduced into a jar of air that has been dried over strong sulphuric acid, chemists have believed that there is some peculiar inertness of carbon monoxide for carbon molecules in the flame, which the presence of steam somehow or other overcomes. The experiments of Bone and Haward,§ in which it was shown that the replacement of even a small proportion of the carbon monoxide by its volumetric equivalent of hydrogen in a normal CO-air explosion at initial pressures of 50 atmospheres had a peculiar accelerating influence upon the maximum pressure developed in the explosion, altogether disproportionate to the volumetric amount of it present, seemed to point to hydrogen being even more potent than its equivalent of steam as the promoter of combustion of carbon monoxide; and it was suggested that its primary

* 'Phil. Mag.' (April, 1902).

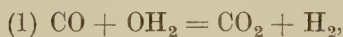
† 'Nature,' vol. 35, p. 165 (1886).

‡ 'Roy. Soc. Proc.,' A, vol. 98, p. 40 (1920).

§ 'Roy. Soc. Proc.,' A, vol. 100, p. 67 (1921).

function might be to resolve continuously the inert O_2 molecule into an active oxidising condition (that is into O atoms and active OH_2) itself being continuously regenerated in the process.

Several different theories have been, from time to time, propounded to account for the peculiar influence of steam (or hydrogen) in the combustion of carbon monoxide. Thus, for example, H. B. Dixon supposed that carbon monoxide reacts with steam (and not O_2) in flames, forming carbon dioxide and liberating hydrogen, which latter immediately combines with the oxygen present, regenerating the steam. According to this supposition, the steam acts as a carrier of oxygen to the carbon monoxide as follows:—



But, as Prof. Bone has already pointed out, such a view, though it may be partially true, does not explain all the facts, and especially the characteristic colour of a carbon-monoxide flame, which is so totally different from that of a hydrogen flame. And, as regards the much-debated question whether in all circumstances CO and O_2 molecules are really incapable of interacting in flames, it may be stated that further experiments are now in progress in his laboratories with a view to obtaining a decisive answer. In the meantime, certain inferences may be drawn from the results of my present experiments, all of which point to there being a definite CO-oxygen spectrum distinct from a CO- OH_2 spectrum.

Experimental.

The carbon monoxide used was prepared by dropping redistilled formic acid into pure concentrated sulphuric acid, and was afterwards passed through a strong solution of caustic potash before being stored in glass holders over a mixture of equal volumes of glycerine and water, pending the actual experiments.

The hydrogen was prepared by the action of pure diluted sulphuric acid upon electrolytic "crescent" zinc (99.98 per cent. purity), supplied by Brunner, Mond & Co., and was purified by being thoroughly scrubbed through hot alkaline solution of potassium permanganate, a treatment which eliminates any traces of hydrocarbon impurity. The spectrograph employed was a small quartz instrument, supplied by Messrs. Bellingham & Stanley, and having a wave-length range from approximately 6000 Å.U. to 2100 Å.U.

First Series.—Spectrographic Comparison of Carbon Monoxide, Hydrogen and Water-Gas Flames.

In this series of experiments the gas or gas mixture was burnt (undried) at a plain silver jet, inserted in the end of a glass tube, the flame being placed directly in front of the slit of the spectrograph for (in each case) a period of an hour and a half, which sufficed to give a good photographic record, Imperial ordinary plates being used. In the first instance, spectrograms were obtained of the flames of a range of combustible gases beginning with 100 carbon monoxide (*i.e.*, pure CO), then passing successively through 92.5/7.5, 80/20, 75/25, 50/50, 27.5/72.5, CO/H₂ to finally 100 (*i.e.*, pure) hydrogen. Some of these are shown in Plate 1, Nos. 1 to 5 inclusive. In this way the effects of gradually replacing carbon monoxide by hydrogen in the flame were brought out.

In Nos. 1 and 5 are reproduced (*a*) the characteristic spectrogram of a pure carbon-monoxide flame, and (*b*) that of a pure hydrogen flame, respectively; whilst the intermediate spectrograms (Nos. 2 to 4 inclusive) are those of flames in which carbon monoxide was progressively replaced by hydrogen, No. 4 being that of a 50 CO/50 H₂ (*i.e.*, “water-gas”) flame.

In the spectrogram (No. 1) of pure undried carbon monoxide can be seen, besides two groups of “steam” lines, a banded radiation, extending from 5000 Å.U. in the visible region to 2200 Å.U. far in the ultra-violet, on which a continuous spectrum is superimposed. Both the banded and the continuous spectra are presumably associated with the characteristic colour and actinic properties of a carbon monoxide flame.

As the carbon monoxide in the burning gas was progressively replaced by hydrogen (Nos. 2 to 4 inclusive), both the banded and the continuous parts of the spectrum rapidly faded away, until with an equimolecular CO-H₂ (“water-gas”) mixture they had nearly all disappeared, leaving only “steam” lines visible in the spectrogram shown in Plate 1, No. 4.* The intensity of these lines increased as the replacement of CO by H₂ continued, until finally they reached a maximum in the spectrum of a pure hydrogen flame (No. 5). Another noteworthy feature of this series of experiments, to which attention is directed, is the rapid shortening of the extreme ultra-violet of the continuous CO-spectrum produced by the progressive addition of hydrogen to the flame; indeed, the progressive suppression of both the continuous and the banded CO-spectra by the successive H₂-additions was by no means uniform over the

* The banded and continuous parts in the “water-gas” spectrogram are just faintly visible in the original negative, but do not show at all in the print (Plate 1, No. 4) obtained from it [25.6.25].

whole radiation, but in the first stages affected the extreme ultra-violet most. In Plate 1, Nos. 6 and 7, are reproduced for comparison the spectrograms of a 75/25 CO-H₂ flame and a 75/25 CO-N₂ flame respectively, from which it can be seen (what is still more clearly brought out in the original negative) that the effect upon the continuous and the banded CO-spectra of the addition of hydrogen is something more than a mere "diluent" effect; because, as compared with the spectrogram of a 75/25 CO-N₂ flame, that of the 75/25 CO-H₂ flame shows the continuous and banded CO-spectra to be decidedly fainter, and at both ends more foreshortened.

It may here be recalled that the flame of "blue" water gas, which usually contains about 40 to 43 per cent. of carbon monoxide and between 45 and 50 per cent. of hydrogen, has much the same appearance as a hydrogen flame, having none of the characteristic colour of a CO flame about it; the reason for this now becomes evident, for, as spectrograph No. 5 shows, in such a flame the particular radiation which gives rise to the characteristic colour of a pure CO flame would be practically all suppressed, leaving that corresponding with the "steam-lines" of a hydrogen flame.

Second Series.—Spectra of Carbon-Monoxide Flames burning in Different Atmospheres.

I next proceeded to compare the spectrograms of pure (undried) carbon-monoxide flames burning in various supporting atmospheres. For this purpose a jet of pure moist carbon monoxide was burnt at the upper enlarged opening (4 mm.) of a 1-mm. bore silica tube A (see fig.), fixed in the vertical axis of the cylindrical glass enclosure B, B, which was fitted with quartz side windows C, C; a side-tube D for the admission of the supporter of combustion; a glass chimney E, communicating with an exit-tube F, to which (if need be) a large pressure-equalizing vessel, manometer, and suction pump could be attached in series. In this way, a carbon-monoxide flame could be maintained in any desired atmosphere and at any pressure, from 1 atmosphere downwards to about 50 mm. In taking the spectrograms, the radiation from the flame, after passing through the quartz window, was focused by means of a quartz lens upon the slit of the spectrograph. The times of exposure were from 45 to 60 minutes, panchromatic plates being used.

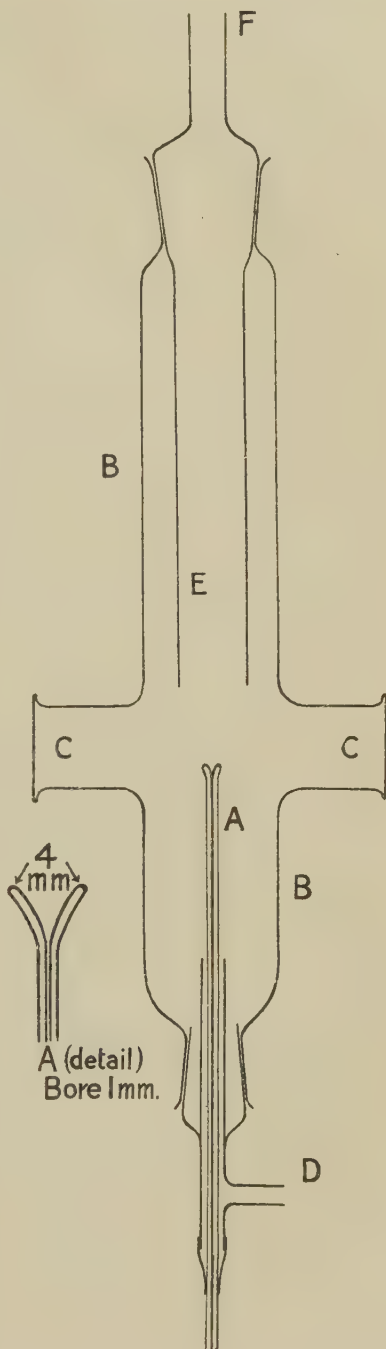
In Plate 2 (Nos. 8 to 13 inclusive) are shown some of the spectrograms obtained from CO flames burning at atmospheric pressures in various supporting media, such as ordinary air (No. 8), argon air (*i.e.*, O₂ + 4Ar, No. 9), undried

oxygen (No. 10), well-dried oxygen* (No. 11), 6 per cent. ozonized oxygen (No. 12), and nitrous oxide (No. 13). There was no material difference between those (Nos. 8 and 9) obtained when the supporting atmosphere was either ordinary air or argon-air, respectively. When, however, it was *undried* oxygen (No. 10), the continuous part of the CO spectrum was much intensified, and prolonged much farther into the ultra-violet. With well-dried oxygen (No. 11) the intensity of the continuous part of the CO spectrum remained undiminished, but the "steam lines" had become very faint indeed. The general character of the CO-oxygen spectrum was not much affected by ozonizing the oxygen (No. 12), although, if anything, it became more distinctly banded towards the extreme ultra-violet end. Finally, the spectrogram obtained with nitrous oxide (No. 13) was much less intense than with oxygen as the supporting atmosphere, and resembled more the CO-air spectrogram.

*Third Series.—Spectra of Carbon-Monoxide
Flames burning in Oxygen at Different
Pressures.*

In Plate 1 (Nos. 14 to 16 inclusive) are shown three of a series of spectrograms obtained when pure (undried) CO flames

* In this experiment, both the CO and the oxygen were dried by passage through concentrated sulphuric acid; in such circumstances it was more difficult than with the undried gases to maintain a continuous flame indefinitely, and it was usually necessary to re-kindle it three or four times during an experiment extending over two hours.



were maintained in atmospheres of undried oxygen at progressively diminishing pressures between 765 and 61 mm.

The chief interest of this series lies in the fact that, as the pressure was progressively reduced, the banded part of the CO spectrum became more distinct, and the continuous part became less intense. Diminution of the pressure, however, did not seem to affect the positions of the bands, but only made them more distinct as the intensity of the continuous spectrum diminished. The "steam-lines" were invariably present in all the spectrograms.

Prof. A. Fowler very kindly carried out measurements of the bands of these CO spectra, and has furnished me with the following description for inclusion in this paper :—

Prof. A. Fowler's Description of the CO-Flame Spectra.—The spectrum of the flame of carbonic oxide burning in air appears to consist of a continuous spectrum of considerable intensity upon which is superposed an ill-defined band spectrum. The ultra-violet bands of water vapour are also a conspicuous feature.

Measurements of the flame bands have been made on a photograph taken with a Hilger quartz spectrograph (size E.2), giving a dispersion of 110 Å per mm. at 5900 and 20 Å per mm. at 3100. It was not found possible to measure the bands under a microscope, and the method adopted was to superpose an ivory scale, divided to hundredths of an inch, on the negative. A comparison spectrum of iron furnished the necessary standards. The resulting wave-lengths are subject to probable errors of at least 2 or 3 Ångström units. The wave-lengths of the bands which appear in the less refrangible part of the spectrum are included in Table I. The intensities tabulated in the second column are rough estimates, on a scale of 3 for the brightest bands, ranging through 2 and 1 for fainter bands to 0 for bands which are just easily perceptible on the negative. Wave numbers, in air, corresponding to the tabulated wave-lengths, are indicated in the third column of the table. The bands continue far beyond the limit of the table, but until some method of producing them with better definition has been found, it scarcely seems worth while to tabulate them, especially as the more refrangible part of the spectrum is complicated by the presence of the bands of water vapour.

Table I.—Band Spectrum of the Carbon Monoxide Flame.

Wave-length.	Intensity.	Wave-number.	Wave-length.	Intensity.	Wave-number.
5555	0	18,002	4528	2	22,085
5490	0	18,210	4485	2	22,297
5430	2	18,416	4437	1	22,538
5392	1	18,546	4413	2	22,669
5348	1	18,699	4307	1	22,899
5318	2	18,804	4344	2	23,020
5278	3	18,947	4335	1	23,068
5226	1	19,135	4307	0	23,218
5169	3	19,346	4298	1	23,267
5129	3	19,497	4260	2	23,474
5082	0	19,677	4235	1	23,613
5026	2	19,897	4203	1	23,793
4981	2	20,076	4154	2	24,073
4932	2	20,276	4141	1	24,149
4896	3	20,425	4130	1	24,213
4851	1	20,614	4104	1	24,366
4817	1	20,760	4093	1	24,432
4798	2	20,842	4073	1	24,552
4769	2	20,969	4063	1	24,612
4724	1	21,169	4045	1	24,722
4659	2	21,464	4034	1	24,789
4654	2	21,487	4008	1	24,950
4608	1	21,701	4000	1	25,000
4598	1	21,782	3966	0	25,214
4577	2	21,848	3942	1	25,368
4557	2	21,944	3911	2	25,569

Regularity in the distribution of many of the bands seems sufficiently evident on inspection of the negative, but on account of the approximate character of the wave-numbers it is somewhat difficult to establish the regularity numerically. The following partial analysis of the spectrum, however, making due allowance for probable errors of the wave-numbers, will serve to indicate that the bands are in all probability distributed in accordance with the general laws which govern the structure of band spectra.

It will be observed that the differences in the columns and rows are as nearly equal as is to be expected from the rough measures at present available, and that the differences are of the same order of magnitude in different parts of the spectrum. It seems clear that the CO flame bands constitute a characteristic spectrum which is quite distinct from the more familiar "oxy-carbon" bands which have been observed in vacuum tubes.

Table II. —Structure of the Band Spectrum of the Carbon Monoxide Flame.

18,416(2)	531	18,947(3)	550	19,497(3)		
388		399		400		
18,804(2)	542	19,346(3)	551	19,897(2)		
				379		
				20,276(2)	566	20,842(2)
20,076(2)	538	20,614(1)	555	21,169(1)		
349		355				
20,425(3)	544	20,969(2)				
335						
20,760(1)						
				21,944(2)	594	22,538(1)
				353		361
		21,701(1)	596	22,297(2)	602	22,899(1)
		384		372		368
21,487(2)	598	22,085(2)	584	22,669(2)	598	23,267(1)
				351		346
				23,020(2)	593	23,613(1)
						24,612(1)
						338
23,218(0)	575	23,793(1)	573	24,366(1)	584	24,950(1)
		356		356		
		24,149(1)	573	24,722(1)		
23,474(2)	599	24,073(2)				
		359				
		24,432(1)	568	25,000(1)	569	25,569(2)
				368		
				25,368(1)		

Concluding Remarks.

My experimental results have been reviewed also by Prof. Bone in conjunction with other work upon the combustion of carbon monoxide now proceeding in his laboratories. He thinks that they are best explained on the supposition that the characteristic banded and continuous parts of the CO-flame spectrum are both of them due to radiation excited by *direct* interactions between carbon monoxide and oxygen, without the intervention of steam, although there is

nothing in them from which it can be inferred whether it is molecular or atomic oxygen that is concerned. The "steam-lines" in the spectrum may be regarded as due to independent interactions between CO and OH₂ molecules in the flame.

In this connection, attention is again directed to the outstanding feature of my results, namely, that the characteristic continuous and banded parts of the CO-flame spectrum not only appear to be quite independent of the "steam-lines," but are rapidly extinguished by successive additions of hydrogen to the burning gas, until they are almost invisible when an equimolecular mixture of carbon monoxide and hydrogen is burnt. On the other hand, the continuous part of the spectrum is greatly intensified when pure (undried) carbon monoxide is burnt in a supporting atmosphere of oxygen at 760 mm. pressure, but as the pressure is reduced its intensity diminishes, until at low pressures the banded part of the spectrum predominates.

The obtaining of a continuous spectrum from the flame of such a gas as carbon monoxide, in which no incandescent solid particles occur, is doubtless rather difficult to understand; but it is nevertheless a well-established fact, which cannot be gainsaid, and must be reckoned with. The experimental evidence shows that it is most probably connected with CO-oxygen interactions in the flame.

The conclusion which seems to follow naturally from these observations is that in the flame of pure (undried) carbon monoxide, two sets of independent interactions occur simultaneously, namely:—(a) direct interactions between carbon monoxide and oxygen, exciting radiations which give rise to the continuous and banded parts of the spectrum, and to the characteristic blue colour of the flame, and (b) interactions between CO and OH₂ molecules, which originate the "steam-lines" in the spectrum. When hydrogen is gradually added to the burning gas, the relative proportions of the first-named interactions diminish rather rapidly, and proportionately more of the CO is burnt by interaction with OH₂-molecules, until when an equimolecular mixture of carbon monoxide and hydrogen is reached, the CO-OH₂ interactions occur to the practical exclusion of the CO-oxygen interactions.

In conclusion, my best thanks are due to Profs. Bone and Fowler for their interest and advice during the research, as well as to the Gas Light & Coke Company of London, for my tenure of their Research Fellowship at the Imperial College of Science and Technology, which has enabled me to devote my whole time to this and cognate researches during the past two years.

DESCRIPTION OF PLATES 1 AND 2.

PLATE 1.

1. Carbon monoxide.			6. { CO 75 per cent.	
2. { CO 92.5 per cent.			H ₂ 25 " "	
H ₂ 7.5 " "			7. { CO 75 " "	
3. { CO 75 " "			N ₂ 25 " "	
H ₂ 25 " "				
4. { CO 50 " "			14. { CO in O ₂ 765 mm. 60 min.	
H ₂ 50 " "			15. { do. 100 " 90 "	
5. H ₂			16. { do. 61 " 150 "	

PLATE 2.

8. CO in air.	11. CO in dried oxygen.
9. CO in argon air.	12. CO in 6 per cent. ozonised oxygen.
10. CO in moist oxygen.	13. CO in nitrous oxide.

The Occurrence of Helium and Neon in Vacuum Tubes.

By R. W. RIDING, Ph.D., and E. C. C. BALY, F.R.S.

(Received 13 June, 1925.)

The formation of helium and neon when the electric discharge is passed through vacuum tubes containing hydrogen was first discovered by Collie and Patterson.* These results were criticised by Lord Rayleigh† and by Merton,‡ who were unable to obtain any evidence of the formation of the rare gases. In a later paper, Collie, Patterson and Masson§ described a further series of experiments, in which they again observed the formation of both helium and neon. Negative results were also recorded by Egerton,|| Piutti and Cardoso,¶ Piutti** and Harkins and Allinson.††

* 'Chem. Soc. Trans.,' vol. 103, p. 419 (1913).

† 'Roy. Soc. Proc.,' A, vol. 89, p. 499 (1914).

‡ 'Roy. Soc. Proc.,' A, vol. 90, p. 549 (1914).

§ 'Roy. Soc. Proc.,' A, vol. 91, p. 30 (1915).

|| 'Roy. Soc. Proc.,' A, vol. 91, p. 180 (1915).

¶ 'J. Chim. Phys.,' vol. 18, p. 81 (1920).

** 'Zeitsch. Elektrochem.,' vol. 28, p. 42 (1922).

†† 'J. Amer. Chem. Soc.,' vol. 46, p. 814 (1924).

In considering the explanation of these very divergent results, mention may be made of the remarkable effects caused by changes in the type of the discharge employed. Collie and his co-workers pointed out the marked differences obtained when the hammer break on the induction coil was replaced by a mercury break, and even by the substitution of new platinum contacts on the hammer break, this change causing a definite decrease in the amount of helium formed. Attention was drawn by one of us (E.C.C.B.)* to the significance of these observations, and the suggestion was made that in order to obtain positive results an optimum type of discharge was necessary and, indeed, that the divergent results obtained might be due to this cause.

Whether this explanation is correct or not, there is no doubt that the question has been left in a very unsatisfactory state, for at the present time there are two entirely contradictory statements, and no solution has been found of a matter which must be considered as of great importance. With the view of putting to the test the above suggestion as to the influence of the type of the discharges, detailed investigation was carried out in these laboratories during 1923 by Dr. R. A. Bailey. Throughout this work uniformly negative results were obtained, no evidence being found of the formation of either helium or neon. It may be noted that the conditions were varied as much as possible in the hopes of recovering the exact type of discharge used by Collie and his co-workers. Since these conditions were unknown we were still not satisfied that these negative results could be accepted as a legitimate criticism of Collie's work, and in December, 1923, we commenced a new series of investigations in which, however, only negative results again were obtained. In these experiments both oxygen and hydrogen were used in the discharge tube. The conclusion was forced on us, therefore, that if the results obtained by Collie were really due to atomic synthesis, there must be present some unknown factor beyond the type of the discharge.

At that time the suggestion was made to us by Prof. Masson that the results obtained by him in conjunction with Collie and Patterson might be due to the disintegration of nitrogen, this element being present in the form of nitride as a surface film on the electrodes. This suggestion at once introduced a fresh point of view, substituting the atomic disintegration of nitrogen for the atomic synthesis of helium from hydrogen. In order to put this suggestion to the test of experiment, a hollow aluminium anticathode was employed which was coated with a thin film of nitride. This anticathode was placed in the focus of a concave cathode, and during the passage of the discharge the gases were

* 'Annual Reports, Chem. Soc.,' p. 45 (1914); p. 30 (1920).

slowly pumped out through a narrow orifice in the anticathode by means of a Sprengel pump. The pressure of the gases in the discharge tube ranged from about 2 mm. to the stage at which the discharge ceased to pass. The induction coil used was capable of giving a 6 in. spark in air and was fitted with a Cox atonic hammer break, since it would seem from Collie and Patterson's work that the discharge obtained with a hammer break is the best.

The first experiments were carried out with hydrogen, but negative results were obtained. On replacing the hydrogen by oxygen a positive result was at once obtained, since after 42 hours discharge a small quantity of helium was formed. Emphasis must be laid on the fact that in many previous experiments with the same induction coil and the same design of discharge tube, without a nitride layer, no trace of rare gases was ever obtained.

On repetition of this experiment, the discharge being passed for longer periods (90 to 100 hours), it was found that hydrogen, helium and neon were formed. It is of considerable interest to note that the relative proportions of helium and neon were the same as those obtained by Collie and Patterson. Altogether 17 spectrum lines due to these gases were measured, and of these one neon line only was not observed by those authors, whilst only one line measured by them was not detected by us. We would again emphasise the fact that no trace of either helium or neon is formed in the absence of the nitride film, and this would seem to exclude the presence of an air leak, since it is not possible to believe in a leak which only occurs when the anticathode is coated with nitride. In addition to this, we have many times confirmed the well known fact that the spectrum of the residual gas left after treatment of air with charcoal cooled in liquid air shows only the spectrum of neon. These results would suggest that the rare gases found by Collie and his co-workers were due to the atomic disintegration of nitrogen and not to synthesis from hydrogen. This conclusion has been confirmed by a number of subsequent experiments which may be briefly described.

In the second series of experiments magnesium nitride was used as the anticathode, and in the first instance a hollow magnesium anticathode was employed, which as before was coated with nitride *in situ*. When the discharge was passed for about 90 hours, both helium and neon were found in the gases. Subsequently magnesium nitride was prepared in the laboratory and used as the anticathode in a modified X-ray apparatus. At first the results obtained seemed very disappointing, since in one only out of several experiments was a small quantity of the rare gases obtained. On the other hand a marked amount of splashing took place, the whole bulb becoming coated

with a thick black layer which could be readily chipped off. Quantitative analysis of this layer revealed the interesting fact that it consisted of approximately two parts of magnesium and one part of aluminium, that is to say that two-thirds of the splash had originated in the anticathode (Mg_3N_2).

At this stage a mercury break was substituted for the hammer break, when after about 60 hours' discharge small quantities of the rare gases were obtained. This result suggests that perhaps after all the effect of using different types of discharge may have been exaggerated. On the other hand, the capriciousness of the results obtained with magnesium nitride demanded an explanation, for we were unable to account for the fact that, whilst being in some cases positive, the results were more frequently negative. Since Collie, Patterson and Masson suggested that occlusion of the rare gases in the electrode splash might explain the negative results obtained by many observers, we examined the splash for the presence of occluded gases.

The discharge tubes, after about 60 hours' passage of the discharge with a mercury break, were disconnected, powdered, and heated in a vacuum. The first samples of gas collected consisted only of oxygen and nitrogen, but on continued heating at about 800° a considerable amount of helium and neon was obtained. This result is of some importance, for it not only shows that the rare gases are occluded in the electrode splash, but also that the effect of a mercury break can only be one of degree.

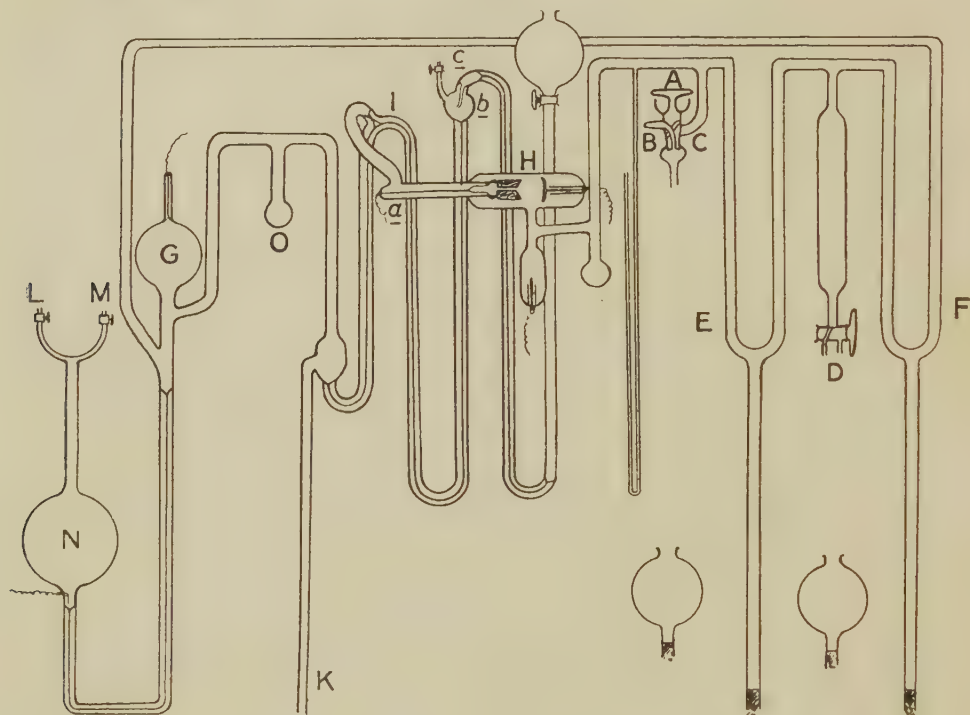
The next series of experiments were carried out with the condensed discharge, using magnesium nitride as the anticathode. Once again considerable splashing took place, and no trace of rare gases was found in the gaseous phase. On heating the splash gently only oxygen and nitrogen were obtained, with no trace of the rare gases. On raising the temperature to the softening point of glass a considerable amount of helium was obtained, this time quite free from neon. Conclusive evidence has thus been gained of the occlusion of the rare gases by the electrode splash to the extent of their complete removal from the gaseous phase. There is little doubt, therefore, that this phenomenon offers a valid explanation of the negative results recorded by so many observers in this field.

Experimental.

A semi-continuous system was used in preference to the usual static type of apparatus, since, although the apparatus is more complex and the consequent difficulties of keeping it in repair many times greater, the discharge conditions are much more varied. It may also be mentioned that since there were no stopcocks in any vital part of the apparatus, and since no transference of gas

from this apparatus to an entirely separate apparatus was required, it possesses advantages over any other large apparatus used in this field of investigation.

The apparatus consisted essentially of two parts, the main apparatus shown in the figure, and the oxygen apparatus, which was connected by the specially



constructed stopcock A. The lower part of this stopcock was sealed to the oxygen apparatus, and by turning the stopcock the sealed tube B could be connected either with the latter or with the tube C. In this way a definite small quantity of oxygen could be admitted into the main apparatus as often as required. The oxygen was prepared by heating potassium permanganate, freed from carbon dioxide by soda-lime, and dried by means of phosphoric oxide. The size of the tube B was so adjusted that the oxygen admitted into the discharge tube exerted a pressure of 2 mm. Since the stopcock was mercury sealed, any atmospheric leak was impossible.

The whole apparatus was connected with a large Toepler pump through one of the arms of the stopcock D, the second arm being used for the admission of air when repairs were necessary to any part of the apparatus. During every experiment all connection between this stopcock and the rest of the apparatus

was cut off by means of the two mercury valves E and F. When these two U-tubes were closed by mercury, the discharge tube H and the examination chamber G were only connected through the Sprengel pump I.

In the first series of experiments the discharge tube was provided with a concave aluminium cathode and an anode placed in a side tube. The anticathode, which was mounted in the focus of the cathode, consisted of a rod of either aluminium or magnesium drilled longitudinally with a small hole. This hole was countersunk so as to expose as large a surface as possible to the cathode stream. This anticathode was fitted tightly on to a fine platinum tube, which was sealed into a glass tube, and this tube in its turn was connected by an internal seal to the tube *a*. The tube *a* was directly connected with the Sprengel pump I, and during the passage of the discharge the oxygen was slowly pumped out through the anticathode and delivered into the examination chamber G. The anticathode was earthed so as to prevent any tendency to repel the cathode stream.

In order to guard against any contamination by air carried mechanically by the mercury supplied to the Sprengel, this mercury was sprayed into the bulb *b*, which was exhausted to the highest point by the Toepler pump, connection thereto being made through the stopcock *c*. The mercury after passage through the Sprengel was collected at K. In the second series of experiments the discharge tube shown was replaced by a tube in which magnesium nitride was exposed to the cathode streams from a flat cathode.

The examination chamber G was provided with a fine capillary tube with a very thin platinum wire sealed in at the upper end. The mercury forms the other electrode, connection being made by an iron wire passing into the mercury reservoir N. The level of the mercury in the examination chamber was regulated by varying the pressure in N, the stopcock L being connected to a filter pump.

The experimental procedure was as follows. The whole apparatus was first exhausted and the cocoa-nut shell charcoal in the bulb O was heated until no further gas was evolved. The discharge was then passed until no further hydrogen was emitted by the two electrodes and the anticathode. This always took a long time; in some cases from three to five weeks were necessary before every trace of the hydrogen lines vanished from the spectrum of the discharge. The discharge tube was then filled with pure nitrogen and the anticathode coated with nitride by passing the discharge with the anticathode as cathode. The whole apparatus was then thoroughly washed out with oxygen, the discharge being passed during the whole operation. The whole apparatus was

then exhausted to the highest point, after which the valves E and F were closed. The fixed amount of oxygen was then admitted into the discharge tube, the Sprengel pump being at the same time started in slow action. After about one hour the pressure was reduced to a point at which the discharge refused to pass, when a further unit quantity of oxygen was admitted, this being continued as long as was desired.

The gas collected in the examination chamber was examined in the way previously described by Collie and Patterson. The bulb O containing the cocoa-nut shell charcoal was immersed in liquid air and left for about one hour. By the cautious admission of air into the reservoir N the mercury was allowed to rise in G until the residual gas was compressed into the capillary tube, where it was examined spectroscopically. A very small induction coil with as weak a current as possible is used for this purpose, as otherwise the rare-gas spectrum is masked by the mercury spectrum.

Discussion of Results.

In view of the fact that positive results have been uniformly obtained with the apparatus described when a surface film or mass of nitride is exposed to bombardment by cathode streams, and this only when the nitride is present, it is difficult to escape from the conclusion that the helium is formed by the disintegration of the nitrogen atom. Apart from the explanation these results offer of the observations recorded by Collie and his co-workers, for it is difficult to avoid the formation of nitride films on metallic electrodes during the preparation and cleaning up of the discharge tubes, it would seem that they confirm and extend Rutherford's proof of the atomic disintegration of nitrogen by means of swiftly moving α -particles. Whereas he was unable by his method to detect the formation of helium when the disintegration takes place, the results here recorded add that final proof which his brilliant experiments necessarily lacked. The production of hydrogen along with the helium is of great interest in this connection, since this is in agreement with the view that the nitrogen atom contains three helium nuclei and two protons.

The results so far described indicate that the effect of the nature of the discharge can be only one of degree, since evidence was obtained of the formation of the rare gases whether a hammer break or mercury break was used, and also when the condensed discharge was employed. The only difference noted in the above experiments was in the relative amounts of the rare gases in the gaseous phase and occluded in the splash. On the other hand, definitely negative results were obtained in two experiments when a larger

induction coil with a hammer-break was used. It is evident, therefore, that there still remains some factor yet to be explained. We believe that this is connected not with the induction coil alone, but with some relation between the coil and the discharge. We are encouraged in this belief by the fact that the length of time during which the discharge must be passed to obtain the rare gases in our experiments is very much larger than was necessary in Collie and Patterson's work. It is very probable that by a fortunate accident these authors used an induction coil which suited their discharge tubes very much better than was the case in our experiments. We hope to investigate this question in greater detail.

The formation of neon along with helium, which was first observed by Collie and Patterson, has been confirmed in the present experiments. The origin of this gas is a mystery, unless it be assumed that the neon has been synthesised from helium. There can be no question but that the helium atoms, when produced by the disintegration of the nitrogen atoms, must be in a highly activated condition. It does not seem improbable that the conditions of activation would be favourable for the synthesis to take place. There is no doubt that neon is actually produced, and, since the origin of both the rare gases is the nitrogen atom, the synthesis of this gas seems to be the only explanation.

Conclusions.

1. When the nitrides of aluminium and magnesium are bombarded by cathode streams the nitrogen atom can be disintegrated, and amongst the products are found helium, hydrogen and neon.

2. The rare gases are occluded in the electrode splash, and may be recovered when the splash is strongly heated.

3. The results described by Collie, Patterson and Masson have been confirmed, and it would seem that the production of helium had its origin in the disintegration of the nitrogen atom.

4. Since the occlusion of the rare gases has in the present experiments been found in many cases to be complete, it is probable that in this phenomenon is to be found the explanation of the negative results recorded by several observers.

5. With a single induction coil giving a 6-inch spark, the rare gases were always obtained, only minor variations in their amounts being observed when the hammer-break was substituted by a mercury-break and when a condensed discharge was used. Negative results were obtained when a larger coil was used.

We beg to express our thanks to Messrs. Brunner, Mond & Co. for a grant which has defrayed the cost of this investigation.

The Absorption Spectra of Mixed Metallic Vapours.—II. The Spectra of Volatile Compounds of Magnesium and the Alkali Metals.

By S. BARRATT, B.A. (Oxon), Dept. of Chemistry, University College, London.

(Communicated by T. R. Merton, F.R.S.—Received June 13, 1925.)

[PLATE 3.]

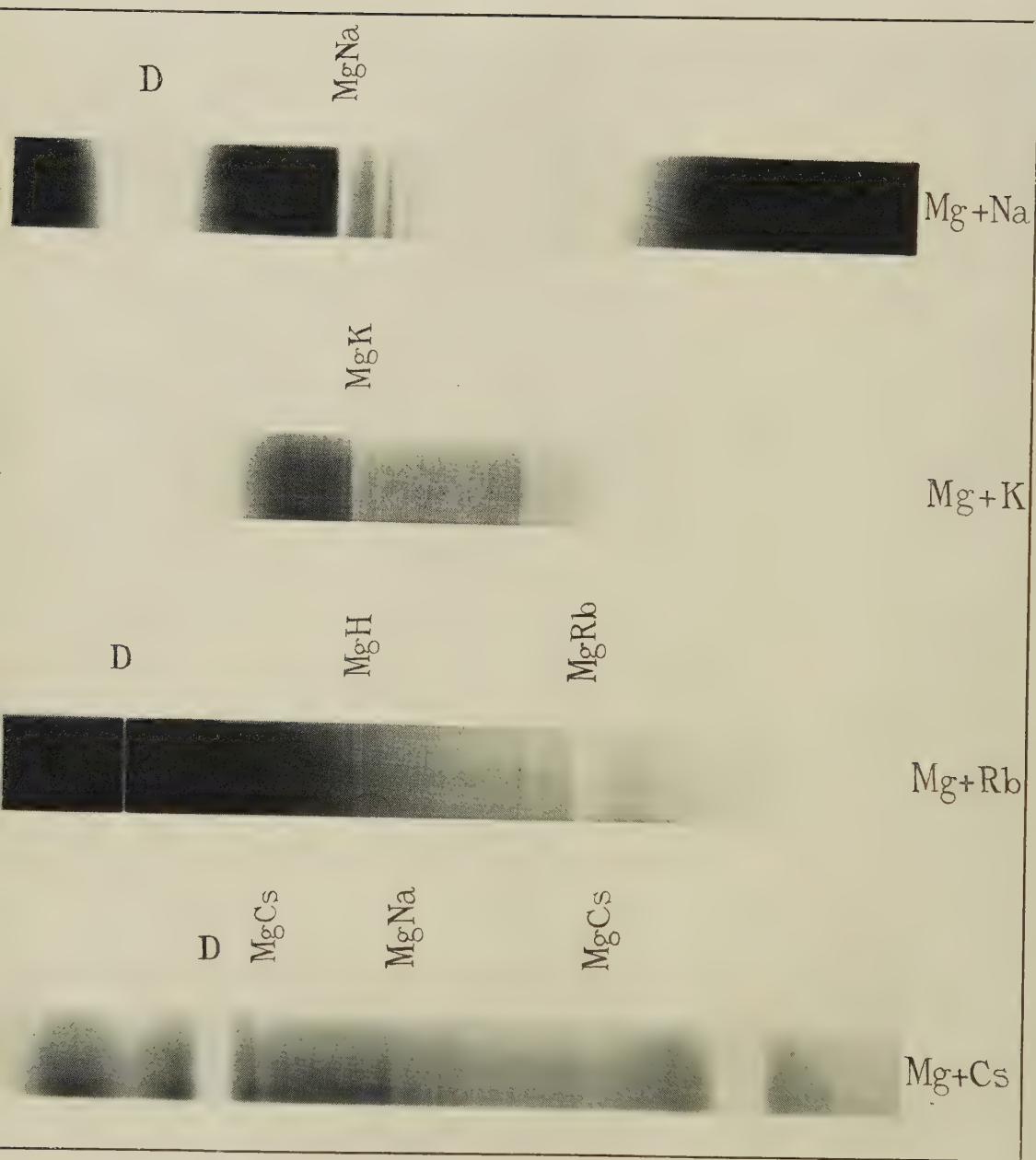
In a previous communication ('Roy. Soc. Proc.,' A, vol. 105, p. 221 (1924)) a band system has been described which is found only in the absorption spectrum of the mixed vapours of sodium and potassium. It was suggested in explanation of this observation that molecules of a volatile compound of the two metals must be present in such mixtures; a supposition which H. G. Smith has since confirmed by comparison of the fine structure of these bands with that of the normal sodium and potassium band spectra ('Roy. Soc. Proc.,' A, vol. 106, p. 400 (1924)).

Bands probably analogous in origin have now been found in the absorption spectra of mixtures of the vapours of magnesium and alkali metals. Two of these spectra—which may be called the "magnesium-sodium" and the "magnesium-potassium" bands—were recorded many years ago by Liveing and Dewar ('Roy. Soc. Proc.,' vol. 27, p. 350 (1878), and 'Collected Papers,' p. 13), but appear to have attracted no subsequent attention. This early description has been amplified, and corresponding absorptions have been shown to exist in mixtures of magnesium with rubidium and caesium.

Experimental.

The metals were volatilised in a steel tube heated by nichrome strip. The ends of the tube were water-cooled, and were closed by glass windows. The tube could be evacuated, or gases admitted, through a side-tube. Some difficulty was encountered in obtaining the mixed vapours of the metals owing to the great interval between the boiling-point of magnesium and those of the alkali-metals.

In vacuo, the alkali metal distilled rapidly to the cooled end of the tube before the vapour pressure of magnesium was appreciable. This difficulty was overcome, in part, by the admission of a hydrogen atmosphere, and also by making use of the temperature inequalities along the furnace tube. Boats



were beaten out of thin sheet iron, filled with magnesium, and placed in the centre of the heated portion of the tube. Similar boats containing either the alkali metals or mixtures of magnesium and alkali chlorides were placed in somewhat cooler sections of the tube. In this way the magnesium and the alkali metal were volatilised simultaneously in spite of the difference in boiling point, and diffusion secured a sufficient degree of mixing for the purposes of the investigation. The spectra were well developed at temperatures of about $1,000^{\circ}$ C. A carbon arc supplied the continuous background, and the spectra were photographed on a Hilger constant-deviation instrument. The observations are therefore limited to the visible region of the spectrum.

The new bands are not of sufficiently open structure for any wave-lengths to be measured satisfactorily under such small dispersion, except those of the band "heads." Secondary absorption maxima were usually visible on the original photographs, but an examination under higher dispersion would be necessary to make a record of these of any value. The wave-lengths given below are the means of values obtained from two or more plates. The iron arc provided the comparison lines.

The "Magnesium-Sodium" Spectrum.

A single band in the green has been observed, adjacent to the sodium band spectrum in this region, but only developed in the appropriate vapour mixture. The band is degraded towards the blue, and the wave-length of the head is 5290.8 Å (Plate 3, fig. 1). This corresponds with Liveing and Dewar's description of "a dark line with ill-defined edges, with a wave-length about 5300 ," which they observed in parallel experiments.

The "Magnesium-Potassium" Spectrum.

The phenomena observed with this mixture are rather more complex. Vapour of moderate density exhibits two bands, one in the red, degraded towards the long wave-length side, with the head at 6549.7 Å, and the other in the blue, degraded towards the short wave-length side, and with the head at 4611.6 Å. In much denser vapour a third band appears in the green, degraded towards the blue, with its head at 5150.4 Å. In the reproduction (Plate 3, fig. 2) only this third band is visible. The structure of the other two is, however, very similar. Liveing and Dewar record a diffuse line at 6580 , which was possibly the first of these bands. They also mention lines at 6475 and 4820 in this mixture. These were not developed in any of the present experiments.

The "Magnesium-Rubidium" Spectrum.

There are absorption bands in the visible due to rubidium itself which have not yet been described, but in addition to these, another band was observed only in the presence of additions of magnesium, with its head at 4728.1 Å degraded towards the blue (Plate 3, fig. 3).

The "Magnesium-Cæsium" Spectrum.

There are two bands peculiar to the spectrum of mixtures of magnesium and cæsium. One shades off on either side of a central maximum at 5706 Å. The other has a head at 4839.2 Å and is degraded towards the blue. Both these bands can be distinguished in Plate 3, fig. 4, though unfortunately no photograph very suitable for reproduction was obtained. The sample of cæsium contained so much sodium as an impurity that the "magnesium sodium" spectrum was also developed, and appears in the plate.

Discussion.

The assignment of these band spectra to the molecules of volatile compounds of magnesium and the various alkali metals is based upon their persistent appearance with mixtures of these metals, and the failure of attempts to produce them in vapours not containing both constituents. Magnesium vapour itself has no band-absorption in the visible, with the exception of the "magnesium hydride" band in the green region, which was consistently observed in the present experiments. The bands could not be detected in the absorptions of the alkali metal vapours unmixed with other metals, and they did not appear in a series of experiments in which calcium vapour replaced the magnesium. The possibility that the spectra were due to tri- or poly-atomic molecules containing hydrogen as well as the metal pairs has also been considered, as an atmosphere of hydrogen was present in all the experiments so far described. The bands have not, however, the wide spacings between individual lines which characterise most hydride spectra, and more direct evidence against this hypothesis has also been obtained from experiments in which an atmosphere of argon replaced the hydrogen in the furnace tube. The argon was admitted after the metals had been freed from occluded hydrogen as far as was possible, by heating and continued pumping, and the "mixed metal" bands were subsequently observed in undiminished intensity. While hydrogen would certainly not be eliminated completely by this procedure, the intensity of the bands as developed in argon makes it highly improbable that hydrogen is necessary for their appearance.

These spectra are the first indication of chemical combination between magnesium and the alkali metals. Investigation of the cooling curves of mixtures of the metals (D. P. Smith, 'Zeit. Anorg. Chem.,' 1907, vol. 56, p. 109; C. H. Matthewson, *ibid.*, 1906, vol. 48, p. 191) has shown that liquid sodium and magnesium are only mutually soluble to the extent of about 2 per cent., while potassium and magnesium are even less miscible. Neither pair of metals gives any indication of compound formation by this method. It is, of course, impossible to determine the molecular formula of the compounds responsible for the absorption spectra from the experiments here described, but an examination of the structure of the bands under higher dispersion would probably give some indication in this matter. It may be remarked that these observations, together with the previous ones on the sodium potassium spectrum, appear to be the first direct evidence for the existence of volatile inter-metallic compounds. Their existence has been postulated in the vapours of certain metallic mixtures, owing to the deposition of definite compounds on cooling, but the inference is by no means a necessary one. It is hoped shortly to investigate such mixtures by the methods employed above.

The spectroscope used in these experiments was purchased with a grant from the Royal Society.

Experiments on the Chemical Activity of Helium.

By E. H. BOOMER, Ph.D., Ramsay Memorial Fellow for Canada
(1923-25).

(Communicated by Prof. Sir E. RUTHERFORD, F.R.S.—Received July 7, 1925.)

Although helium is chemically inert under ordinary conditions, evidence obtained in recent years suggests the possibility that under special conditions it may exhibit chemical activity. Particularly under the influence of the electric discharge, helium atoms may be brought into a special state in which they possess the power of uniting with other elements to form compounds either of a fugitive or permanent character. At the suggestion of Prof. Sir E. Rutherford, a search has been made to find whether evidence could be obtained of the formation of such compounds under the action of intense electronic bombardment. It may be stated at this point that strong evidence has been obtained which leads to the belief that under certain conditions helium forms a tungsten helide of the formula WHe_2 , a black solid at ordinary temperatures which decomposes at high temperatures. Some evidence has also been obtained that the vapours of mercury, iodine, phosphorus and sulphur unite with helium, forming substances which are stable at liquid-air temperatures and decompose at slightly higher temperatures.

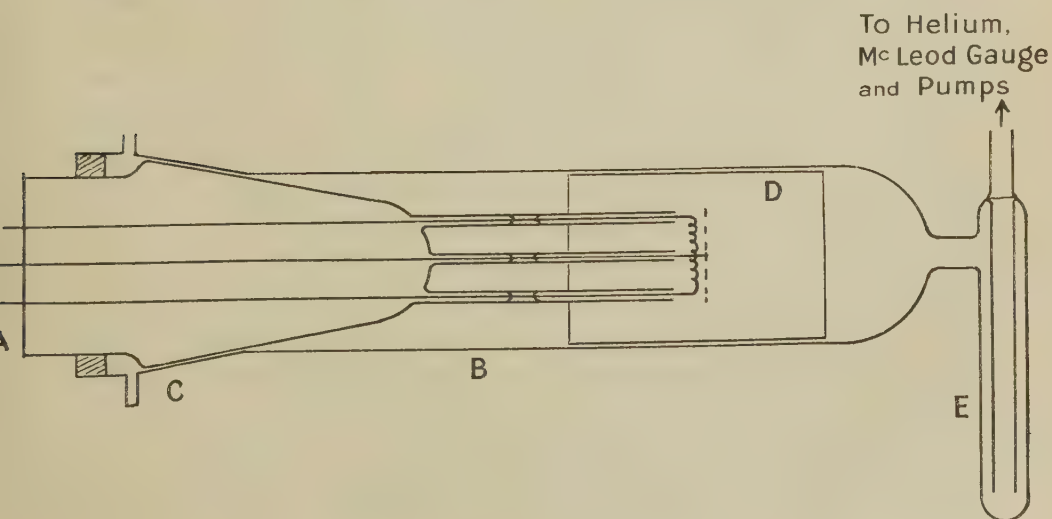
Before discussing the actual experiments, it is desirable to give a brief account of previous observations on the problem. Attention has been drawn on many occasions to peculiarities in the behaviour and occurrence of helium. It is known that helium occurs in small amount in widely different substances, and in many cases this is accounted for by the presence of radioactive matter. Strutt (1), however, has drawn attention to a very remarkable case, in which helium is occluded in very considerable amounts in beryl, where no appreciable radioactive matter is to be found. Many years ago Berthelot (2) believed he had obtained helium in the combined state by subjecting mixtures of helium and the vapours of carbon disulphide or benzene to the silent electric discharge. Strutt (3) investigated the point, and on repeating Berthelot's work failed to confirm his results. Special reference should be made to the absorption of helium in discharge tubes (4) by the electrodes, the sputtered metal and the glass. It is generally agreed that the helium is not chemically retained, but that the phenomena are due to occlusion. In some instances (5) helium

has been found to appear in a discharge tube after running it for some time, and its origin is not yet clear.

Since the formulation of Bohr's theory, the question of the exact arrangement of the electrons in helium has been a subject of much discussion. It is generally agreed that the helium atom in its normal state has two electrons moving in 1.1 crossed orbits with an ionisation potential of about 24.5 volts. It is also believed that an electron is displaced at 20.4 volts to an orbit co-planar with that of the remaining electron, thus forming what is known as "metastable" helium. The suggestion that helium may combine with itself when in this condition to form molecules which give rise to the band spectrum of helium has been put forward by Sommerfeld (6) and others. Much experimental work has been done on the subject by Franck (7) and others which need not be referred to here. It will suffice to say that the "metastable" helium resembles hydrogen in that the displaced electron is relatively far from the nucleus and might be expected to show some chemical activity.

Experimental Arrangement.

A large number of experiments were carried out which gave no result beyond showing that helium is occluded in the walls and electrodes of the apparatus. We shall only give here the final arrangement utilised to obtain the tungsten helide. The essential condition is an intense electronic bombardment of helium at low pressures in the presence of a heated tungsten filament. The type of discharge used was suggested by the work of Stead (8) on the



properties of its glow, and is obtained by placing a tungsten filament within 1 or 2 mm. of a very open grid.

In the figure the tube A, carrying the filament and grid is fitted into the tube B by means of the mercury sealed ground-glass joint C. This joint was very finely ground, and did not permit mercury vapour to pass through it. The inner tube D surrounds the filament and grid, and is placed so as to collect the material deposited from the discharge. This tube can be removed when the tube A is taken out and the material on it examined. The tube B was connected through the liquid-air trap E to a McLeod gauge, a spectrum tube and a helium-supply. The evacuation of the apparatus was carried out by a mercury diffusion pump. The McLeod gauge was used to follow the pressure change accurately, and the volume of the apparatus was carefully determined in order to know the amount of helium used in an experiment. The helium supply was 99.5 per cent. pure, and was further purified by charcoal cooled in liquid air until, on examination in a Hilger constant deviation spectrometer, only the helium lines were visible.

The procedure was as follows :—The tube D and the filament were carefully weighed and placed in position. If desired, mercury was introduced into the tube before putting the tube A in position. The evacuation was then carried out, and at the same time the apparatus was heated with a Bunsen flame. Liquid air was put around the trap E, and, with the apparatus open to the pump, a heavy discharge started from the heated filament to the grid. This discharge, particularly if mercury vapour was present, rapidly removed the gas from the walls and electrodes, and when no more gas came off the evacuation was discontinued. Pure helium was then admitted to the apparatus to the required pressure, generally about 4 mm. of mercury, and the discharge started at 1,000 volts and 5 to 10 milliamperes. The pressure fluctuated a little during the first ten minutes and then steadily decreased, being measured at regular intervals by the McLeod gauge. The spectrum of the helium was examined from time to time by the spectrometer, both in the glow and in the spectrum tube, to show that it remained pure.

When the pressure reached the neighbourhood of 0.1 mm. of Hg the discharge was stopped, and the filament and inner tube removed, weighed, and the deposit analysed. The amount of helium that had disappeared was easily calculated from the pressure change and the volume of the apparatus to better than 1 per cent., and the loss in weight of the filament was correct to 5 per cent., as was also the measurement of the helium evolved from the tube. The experiments without exception agreed within these limits.

Experimental Results.

In the results that follow, the relations between the loss in weight of the filament and the amount of helium that disappeared were obtained with leads of the four materials copper, nickel, tungsten and aluminium, but the analysis of the deposit on the collecting tube was carried out when aluminium and in a few cases copper leads were used. In general, the atomic ratio between the loss in weight of the filament and the loss of helium was 1 : 2, but it was found that the proportion of tungsten could be increased by having a large amount of mercury present. No experiment was made in which the proportion of tungsten, within the limit of error, was less than in the ratio WHe_2 .

As an example of the agreement obtained we may quote the number of helium atoms which disappeared for each tungsten atom in the last 10 experiments : 2.1, 2.1, 1.9, 0.8, 0.9, 2.0, 1.1, 0.6, 0.6, 1.9. In the fourth, fifth, seventh, eighth, and ninth examples a large amount of mercury was present in the tube, and the proportion of tungsten was found to be much greater than in WHe_2 . That the evaporation of the filament paralleled the disappearance of the helium was shown by measurements of the resistance of the filament. In the early part of the experiment, before the filament became appreciably uneven, the increase in its resistance, which is proportional to its loss in weight, was found to vary exactly as the decrease in pressure of the helium.

The analysis of the black deposit on the collecting tube and on the small glass tubes carrying the leads agreed with the results obtained from the loss in weight of the filament. The amount of tungsten on the lead tubes was small and unweighable, but the helium, however, was obtained in several cases by heating them, and was found to vary between 4 and 7 per cent. of the total that had disappeared. The remainder of the helium was always found on the large tube. It was collected by heating the tube, the helium all coming off suddenly at a temperature about that of the softening point of glass. The metal sputtered from the leads was dissolved off, and the tungsten remaining on the glass was weighed and always found to equal the loss in weight of the filament.

It was found that in 20 per cent. nitric acid or potassium hydroxide the helium was liberated rapidly and completely in the form of a cloud of small but easily visible bubbles. The potassium hydroxide removed the tungsten and also the aluminium when present. The nitric acid dissolved no aluminium during the time the tube was in the acid (about 20 seconds), but did remove the tungsten. When the tungsten was present in the ratio 1W to 2He all the

tungsten was dissolved or changed to tungstic oxide; but if the ratio of tungsten to helium was greater than this, it was found by actual weighing that only the amount of tungsten necessary to form WHe_2 was dissolved, the tungsten in excess of this remaining on the glass in the ordinary metallic state.

The deposit as formed on the tube was quite different in lustre from that of the metallic tungsten which was left behind after the solution of the compound. It was found that the amount of mercury in the deposit, if any, was very small and could not be weighed. These experiments were repeated many times and always gave the same result. As examples of the agreement reached, the analyses obtained from the five cases previously given, where the tungsten was in excess, are: 1.9, 2.1, 1.8, and 1.9. A typical example of the above procedure, using aluminium leads and a small amount of mercury, may be given here to illustrate the quantities involved.

Current	5 ma.
Voltage	1,000.
Original pressure of helium	0.418 mm.
End pressure of helium	0.058 mm.
Loss in weight of filament	0.0011 gr.
Loss of helium	257 c.mm.
Atomic ratio	1 : 1.9.
Weight of tube cleaned	40.9845 gr.
Weight of tube with deposit	40.9867.
Weight of deposit	0.0022.
Weight of tube after treatment with nitric acid	40.9856.
Tungsten removed	0.0011 gr.
Helium evolved	240 c.mm.
Atomic ratio	1 : 1.8.

In view of the good concordance of these results, obtained under varying conditions, it is difficult to avoid the conclusion that we are dealing here with a definite compound of helium and tungsten of the formula WHe_2 . We have seen also that the chemical properties of the compound are distinctly different from those of tungsten.

Effect of Pressure, Voltage, Current, etc.

Several interesting points arose during the experiments on the effects of various factors on the progress of the reaction. The disappearance of helium was found to depend largely on the pressure. Above 0.5 mm. of mercury

the helium did not disappear at an appreciable rate, and below 0.05 mm. the rate was so slow as to be difficult to measure with certainty. In the range of pressure found 0.1 to 0.45 mm. the rate of disappearance was greatest and nearly constant, reaching under the best experimental conditions 4 to 5 c.mm. of helium at N.T.P. per minute.

The voltage generally used was 1,000, and was never higher. The effect of lowering the voltage was investigated, and it was found that the velocity of the reaction was decreased until at 200 volts it became very small. The current between the filaments and grid also controlled the velocity of the reaction—above 20 milliamps. or below 2 milliamps. the reaction proceeded slowly. From 5 to 10 milliamps. were found to be most suitable. The reaction obviously depended largely upon the character of the discharge. The most satisfactory conditions were a pressure less than 0.45 mm. of mercury, with a potential of 1,000 volts and a current of 5 to 10 milliamps. Under these conditions a bright glow filled the entire tube, in which only the orthohelium and parhelium series could be seen in the spectrometer, together with mercury lines if mercury was present.

Both the material of which the leads consisted and the presence of mercury vapour had a marked effect on the rate of the reaction. In the absence of mercury vapour, using copper, nickel or tungsten leads, which all sputter heavily, the velocity varied from 0.5 to 1.0 c.mm. of helium per minute. On introducing mercury vapour the velocity of the reaction increased and reached on occasions 5 c.mm. of helium per minute at 0.02 mm.-Hg. pressure. In the majority of experiments aluminium leads were used, because of the small amount of sputtering from them, and it was found that in these cases the helium did not disappear at an appreciable rate in the absence of mercury vapour.

The rôle of the mercury vapour is difficult to explain. It does not appear to have any appreciable effect on the sputtering from the leads. An interesting observation was made, however, which may bear on this point. In the preliminary discharge for cleaning up the tube when no helium was present the presence of mercury vapour exerted a marked effect on the rate of volatilisation of tungsten. In the absence of mercury vapour the loss in weight was less than 0.05 mg. per hour. When the pressure of mercury was raised by slightly warming a drop of mercury in the tube the volatilisation of tungsten greatly increased, and for a pressure of about 0.02 mm. the rate of volatilisation was 0.5 mgm. per hour, the tungsten being deposited on the walls in the metallic state. We are not aware that this peculiar effect of

mercury in promoting volatilisation has been noticed before. This may be the explanation of the effect of mercury vapour on the reaction, but it may be that it plays a more primary part in the ultimate formation of the compound.

Unstable Compounds.

In the preliminary work with this type of discharge some evidence of the existence of unstable combinations between helium and various substances was obtained. The apparatus was modified to permit a surface at the temperature of liquid air to be in the glow, by means of a vertical side-tube carrying an inner tube with a closed end, placed 1 cm. from the grid on the side away from the filament. Liquid air was placed in the tube and a discharge started through mixtures of helium and the vapours of mercury, iodine, sulphur, and phosphorus. A continuous supply of these vapours was necessary, because of the rapidity with which they were condensed on the cold surface. Mixtures of helium and hydrogen and nitrogen were also investigated in this way, but led to no result, the second gas being quickly cleaned up without loss of helium.

The helium disappeared rapidly, however, in the other four cases and was found to be on the cold inner tube. Voltages from 200 to 1,000 and currents up to 40 milliamps. were used, at pressure from 0.1 to 0.2 mm. of Hg. The helium disappeared rapidly when the glow was brightest around the liquid-air tube, at 1,000 volts and 20 milliamps. the rate varying from 5 to 10 c.mm. per minute. The disappearance of the helium was undoubtedly due to the discharge, and did not require the presence of mercury-vapour in the cases of phosphorus, sulphur, and iodine. In the absence of the glow no helium was removed at all, even when large amounts of the second components were allowed to condense on the cold surface. A discharge between a filament and plate with the whole immersed in liquid air and having a continuous supply of the vapours, failed to show any effect other than a small amount of occlusion.

The pressure of helium dropped to 0.005 mm. of mercury and remained constant as long as liquid air was present. On allowing the liquid air to evaporate and the tube to warm up, the pressure rose very slowly, until at a definite temperature, which was far below the freezing-points of the vapours used, nearly all the helium was suddenly liberated. Such a result would not be expected if the helium were merely occluded and not combined with the condensed vapour. With mercury and iodine this temperature was nearly the same, and about -70°C. , while with phosphorus or sulphur the decomposition occurred at approximately -125°C. A small amount of helium always disappeared permanently, and may have been due to occlusion or the

formation of the tungsten compound. Experimental difficulties, such as the unstable character of the substance and the great excess of the solidified vapour, prevented the analysis of these bodies from being carried out.

Summary.

A brief account of the previous evidence indicating that helium may be chemically active has been given. Experiments have been made with an intense electronic discharge from a tungsten filament in helium at low pressures, which led to the belief that a distinct and stable compound of the formula WHe_2 exists. The various factors influencing the reaction, such as voltage, current, pressure, the metals of which the leads are made and the presence of mercury vapour, have been investigated.

Evidence has also been obtained that helium unites with the vapours of mercury, iodine, phosphorus, and sulphur to form compounds which are stable only at low temperatures.

In conclusion, I wish to express my thanks to Prof. Sir Ernest Rutherford both for his suggestions and his continued interest in the work, and for providing the means by which the work could be carried out in his laboratory. I also wish to acknowledge my gratitude to the Research Council of Canada for granting me the Ramsay Memorial Fellowship for two years, which enabled the work to be carried out.

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- (1) 'Roy. Soc. Proc.,' A, vol. 80, pp. 56 and 572.
 - (2) 'Ann. de Chim. et de Phys.,' (7) vol. 11, p. 15.
 - (3) 'Roy. Soc. Proc.,' A, vol. 87, p. 381.
 - (4) 'Roy. Soc. Proc.,' A, vol. 79, p. 92, and vol. 80, p. 92.
 - (5) 'Trans. Chem. Soc.,' 1913, vol. 103, p. 419.
 - (6) Sommerfeld, 'Atombau und Spektrallinien,' p. 563.
 - (7) 'Zeit. für Phys.,' vol. 1, pp. 54 and 320 (1920).
 - (8) 'Phil. Mag.,' November, 1924.
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Further Experiments on the Absorption and Scattering of γ -Rays.

By N. AHMAD, Ph.D., Peterhouse, Cambridge.

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The absorption and scattering of γ -rays by elements has already formed the subject of two papers published recently in these proceedings.* The objects of the experiments described in this paper were (1) to extend the absorption measurements, especially in the more important direction of the extremely short waves emitted by RaC, and (2) to make a thorough investigation, with special reference to Compton's theory, of the scattering by matter of these high-frequency radiations.

It was shown in the papers referred to that the absorption of γ -rays from RaB + C, filtered through 1 cm. of lead, is closely expressed by relations similar to those which hold for X-rays. Estimates of the mean-effective wave-length of the beam placed the value at about 0.02 Å.U. Now, it is well known from the crystal analysis of Rutherford and Andrade,† and the β -ray magnetic spectra measurements of Ellis,‡ and Ellis and Skinner,§ that the γ -rays emitted by radium products cover a wide range of wave-length—roughly, from 1.0 to 0.005 Å.U. It is, however, uncertain whether the very short waves obey the same general laws of absorption as the ordinary X-rays. Direct measurements on a few selected homogeneous rays, though capable of yielding most important results, are unfortunately impracticable. The problem has, therefore, been attacked by the less direct method of measuring accurately the absorption of a complex beam, successively hardened by means of five suitable filters. It will be shown that in every case the absorption of γ -rays obeys the same general law as has already been found. The measurements also throw some light on the spectral distribution of energy in the beam.

It was further shown that the classical theory was quite incompetent to deal with the scattering of γ -rays in a satisfactory fashion, and that these rays, on account of their short wave-lengths, should provide a suitable means

* Ahmad, 'Roy. Soc. Proc.,' A, vol. 105, p. 507 (1924); Ahmad and Stoner, 'Roy. Soc. Proc.,' A, vol. 106, p. 8 (1924).

† Rutherford and Andrade, 'Phil. Mag.,' vol. 27, p. 854 (1914).

‡ Ellis, 'Proc. Camb. Phil. Soc.,' vol. 22, p. 369 (1924).

§ Ellis and Skinner, 'Roy. Soc. Proc.,' A, vol. 105, p. 165 (1924).

for testing the alternative hypothesis put forward independently by Compton* and Debye.† Experiments have been carried out with a view to applying two distinct tests. In the first place, the total absorption due to scattering—for brevity called “scattering absorption”—as given by the theory was compared with that given by the scattering term of the general absorption relation characterising each beam. Secondly, by means of an ionisation chamber capable of revolving about the middle point of the radiator, the intensity of the rays scattered within a small cone was directly measured and compared with that given by theory. It may at once be mentioned that the results of these experiments are in general agreement with the formulæ obtained by Compton on a classico-quantum basis, although the validity of his treatment is questionable.‡

In addition, some measurements were carried out on the absorbability in aluminium of the scattered rays. The results were in fair agreement with Compton's theory, but the experiments were not sufficiently accurate to be considered in detail in this paper.

General Considerations.

(1) *The Absorbers.*—The characteristic features of the previous work, namely, the use of equivalent thicknesses of absorbing material and of double lead “slits,” have been strictly adhered to. For reasons already given, the vital importance of these precautions cannot be over-emphasised. The absorbers themselves were circular plates, of about 7 cm. diameter, with thicknesses adjusted so as to produce an absorption of about 20 per cent. Since a large amount of experimental work was required for each absorber, four typical elements were selected, viz., Al, Cu, Sn and Pb.

(2) *The Filters.*—In order to avoid complications due to the excitation of characteristic radiation, elements with large atomic numbers were at first avoided. But, later, finding that even for large absorption, a lighter element like iron did not produce enough hardening, lead and mercury were also used. The thicknesses of the various filters were as follows :—

Fe 0.05, 2.5, 6.5 cm.

Pb 1.0 cm.

Hg 3.4 cm.

* Compton, ‘Phys. Rev.’, vol. 21, p. 483 (1923).

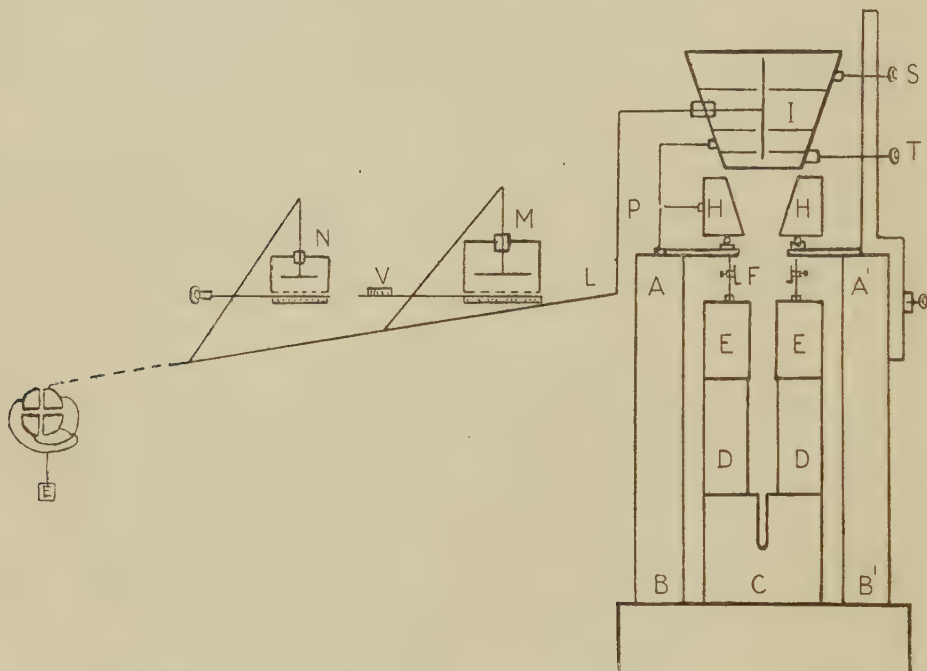
† Debye, ‘Phys. Zeit.’, vol. 24, p. 161 (1923).

‡ See Woo, ‘Phys. Rev.’, vol. 25, p. 444 (1925).

(3) *The radioactive sources* were either a radium standard of 7.86 mgm., or tubes of similar shape containing 60-100 mgms. emanation (radon). The half-value period of the latter was taken at 3.85 days.

The Apparatus.

The apparatus is shown in the figure. The source was placed in a central hole in the lead cylinder C, which rested on a brick platform between two brick walls AB, A'B'. The filters were placed directly over the source inside



a hole in a second lead cylinder D. A third lead cylinder E, with a slightly smaller hole, formed the first "slit," and gave a well-defined beam, with semi-vertical angle of about 6° . The absorbers were placed in the bottomless aluminium tray F, which could slide vertically on two uprights fixed in E. The lead block H, in the middle of which a conical hole formed the second "slit," rested on a V-shaped groove and a plane surface projecting inwards, as shown, from the brick walls. When H was in position, all the scattered rays except those within a cone of semi-vertical angle of 18° were stopped from entering the ionisation chamber. In scattering experiments H was moved aside in the direction opposite to that in which the chamber was revolved.

The chamber I was made entirely of lead sheet, the face and walls being 1.5 mm. and 5.0 mm. thick respectively. It was divided inside into four compartments by lead plates 1.5, 3.0, and 4.5 mm. thick; the depth of the compartments being 2, 3, 4 and 5 cm. This was done in order to make sure that all wave-lengths should have an equal chance of being absorbed.

The ionisation chamber was mainly supported from the ceiling by means of a differential pulley arrangement (not shown). Its rotation was guided by two stout rods S, T, which passed through two quadrants cut in a strong wooden board which was clamped firmly to one of the brick walls. The electrode wire turned at the point L, where a sulphur plug was inserted to keep it firm. The correct positions of the chamber and slit H were fixed once for all by the pin-points at P.

The rectangular Bronson uranium resistance, M, was essentially similar to that described in the first paper, but the vernier V was much finer—being capable of reading to 0.001 mm. The dish containing U_3O_8 was covered with thin aluminium foil to stop the α -particles, the ionisation produced by β -rays alone being utilised.* The surface of the oxide was made very smooth, and the β -rays had to pass through a window with parallel sides. Thus, except for the first few millimetres, the ionisation currents supplied by the uranium resistance should be strictly proportional to the vernier readings. Careful calibrations and tests showed that this was actually the case. The zero of the vernier scale was fixed at 1.700 cm.

Another smaller uranium resistance, N, was used to balance the natural leak. All ebonite plugs had guard rings. The electrode wires were carefully shielded and connected as shown to lead to the sensitive electrometer. The ionisation Chamber I and the uranium resistance M were charged to — 120 volts. The small resistance N was charged to + 80 volts.

(a) *The absorption experiments.*—In a typical experiment the procedure was as follows:—Without the source the natural leak was balanced against the small resistance N. With the source covered by the suitable filter, the resistance M was adjusted for no deflection. Let the corresponding vernier reading be a cm. The absorber was now placed in its correct position and a second null point adjustment made. Let the new vernier reading be denoted

* It may prove useful to future workers to note that the ionisation produced by α -rays is too fluctuating to be suitable in balance methods. This is true even when the period of the detecting instrument (in this case a Compton electrometer) is of the order of 10–20 seconds.

by b cm. Then the mass absorption coefficient (μ/ρ) is at once seen to be given by

$$e^{-(\mu/\rho) \cdot m} = \frac{b-1.700}{a-1.700}, \quad (1)$$

where m is the mass per unit area of the absorber. Each null point reading lasted from 3 to 5 minutes, and was repeated several times. In this way it was possible to measure within 2 div./min., the total current being of the order of 2500 div./min. The absorbers were so held that the distance between their centres and the face of the chamber was constant. Each experiment was repeated at least twice.

(b) *The Scattering experiments.*—Measurements on the intensity of the scattered rays were made with the axis of the ionisation chamber inclined at 40° , 60° , to the direction of the primary beam. The ionisation effect of the scattered rays was measured directly as the effects were too small—of the order of 30-150 div./min.—to use a balance method with advantage. Each reading was repeated about 15 times and every experiment twice. The emanation was allowed to decay until the intensity of the primary beam was of the right order to be measured. The electrometer was used at a sensitivity of 9000—10,000 div./volt.

Results.

The results of the absorption and scattering experiments will be discussed separately, such general remarks as refer to both being reserved for the end. This method of treatment is the more desirable, as, on account of difference in method, the measurements on absorption are considerably more accurate than those on scattering.

Absorption Results.

The experimental values of the mass-absorption co-efficients and their means are given in Table I. At the head of each column is shown the nature and thickness of the filter. The percentage absorption of the primary beam in the filters is given in column I of Table II, its relative intensity after passing through them being shown in column II.

The mean probable error, as will be seen from Table I, rarely exceeds 1 per cent. It is generally of the order of 1 in 200.

Table I.—Mass-Absorption Co-efficients.

Ab- sorbers.	Fe 0.50 cm.	Fe 2.50 cm.	Fe 6.50 cm.	Pb 1.0 cm.	Hg 3.41 cm.
Al	0.0568 0.0570	0.0539 0.0546	0.0540 0.0540	0.0515 0.0514	0.0515 0.0511
Cu	0.0550 0.0552	0.0552 0.0523	0.0526 0.0539	0.0513 0.0508	0.0500 0.0507
Sn	0.0582 0.0581	0.0542 0.0548	0.0531 0.0532	0.0501 0.0496	0.0486 0.0490
Pb	0.0821 0.0817	0.0740 0.0737	0.0695 0.0687	0.0629 0.0623	0.0612 0.0606

Table II.

Filter.	I	II
No filter	0.0	100.0
Fe 0.5 cm.	16.7	83.3
„ 2.5 „	59.0	41.0
„ 6.5 „	90.1	9.9
Pb 1.0 „	54.5	45.5
Hg 3.4 „	91.6	8.4

In analysing the results, the same plan will be adopted as before. A few facts, however, which readily emerge, will be briefly noted first.

It will be seen from Table I that as the thickness of the filter is increased, μ rapidly tends to assume a constant value. This is most marked for light absorbers and heavy filters. Thus the increased absorption of the primary beam, amounting to 37 per cent., resulting from the substitution of the Hg for the Pb filter, produces no measurable reduction in (μ/ρ) in Al, while it reduces that in lead by less than 3 per cent. The effect with light filters is not so pronounced, but it is unmistakably present.

These results are not only in general agreement with those of previous workers,* but, as will be shown, go somewhat further. They point to the conclusion that a considerable fraction of the energy of γ -rays from RaB + C is concentrated in a small range of wave-lengths. The longer waves are readily eliminated,

* *E.g.* Soddy and Russell, Tuomikoski, etc. For full references see the first paper.

especially by the heavy elements in which the fluorescent absorption plays an important rôle. This point is well brought out by a comparison of the values in the fourth and fifth columns of Table I. Though the Pb filter absorbs only about half as much of the primary beam as the Fe filter, it reduces the mean effective wave-length more, as shown by the smaller values of μ/ρ .

The Absorption Formulæ and the Mean-effective Wave-lengths.

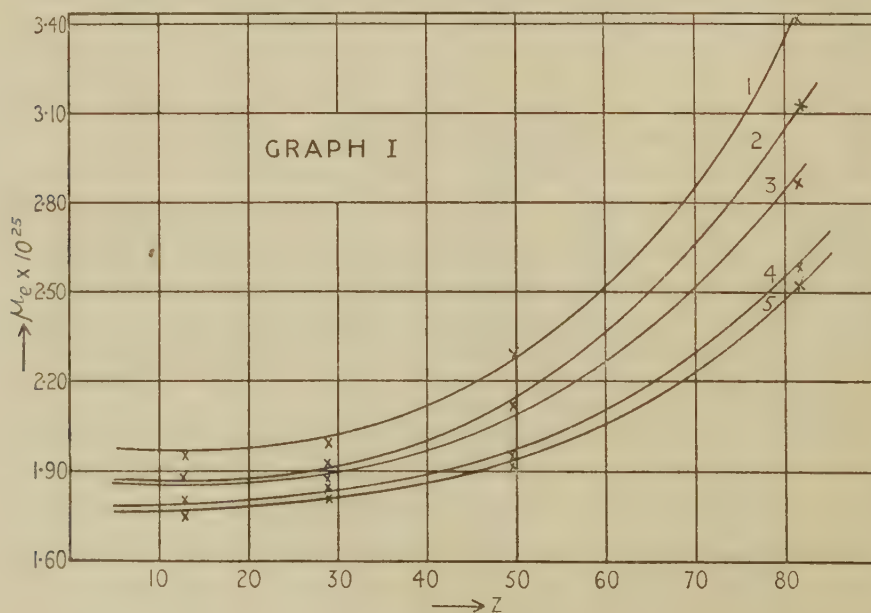
We shall now consider the *absorption per electron* (μ_e) as given by

$$\mu_e = \frac{\mu}{\rho} \cdot \frac{1}{N} \cdot \frac{Z}{A}, \quad (2)$$

where N is Avogadro's number (6.06×10^{23}), Z the atomic number and A the atomic weight of the absorber. The calculated values of μ_e are given in Table III, and plotted against Z in Graph I. The curves are similar to one

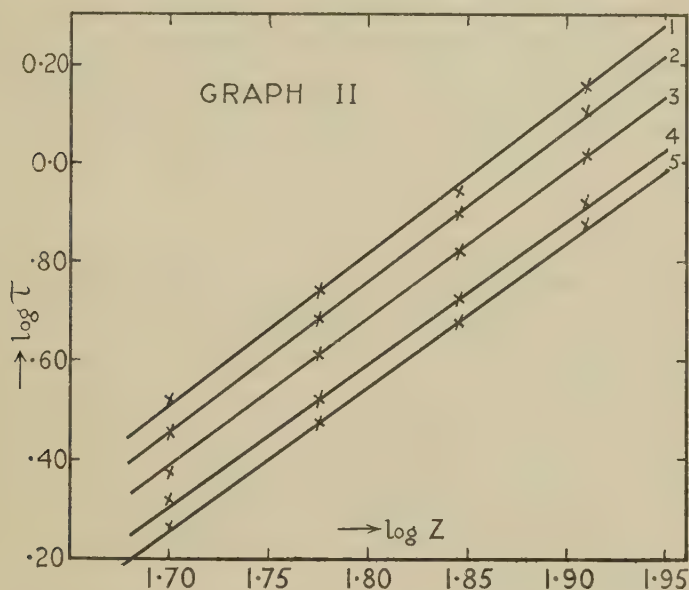
Table III.—Absorption per electron $\times 10^{25}$.

Absorbers.	Filters.				
	Fe 0.5 cm.	Fe 2.5 cm.	Fe 6.5 cm.	Pb 1.0 cm.	Hg 3.4 cm.
Al.....	1.958	1.873	1.858	1.769	1.765
Cu.....	1.997	1.888	1.913	1.845	1.823
Sn.....	2.280	2.135	2.028	1.965	1.912
Pb.....	3.415	3.078	2.881	2.610	2.540



another, the fact that they are all smooth justifying the selection of a small number of absorbers, provided the absorption co-efficients are measured accurately.

It will be seen that with increasing filter thickness, the initial straight parts of the curves tend to merge into one another, while the rise for large Z becomes less and less rapid. This is due to a decrease in the relative contribution of the fluorescent absorption with decrease in the mean-effective wave-length of the beam. In order to study these effects quantitatively we shall, as before, subtract the values for Al from the ordinates of the curve. The differences are plotted logarithmically against Z in Graph II. The slope in each case is



very nearly equal to 3, the actual values lying between 2.95 and 3.05. This gives, for the general equation to the curves in Graph I,

$$(\mu_e)_n = A_n + B_n Z^3, \quad \text{or} \quad (\mu_a)_n = A_n Z + B_n Z^4, \quad (3)$$

where μ_a represents the *absorption per atom* and n denotes the number of the curve. The values of the coefficients A , B for $n = 1, 2 \dots 5$ are given in Table IV.

Table IV.

I. n	II. $A \times 10^{25}$	III. $B \times 10^{31}$
1	1.958	2.621
2	1.868	2.621
3	1.853	1.908
4	1.765	1.528
5	1.760	1.415

It has been established in the two previous communications that the first and second terms on the right side in formula (3) *must* be regarded as representing scattering and fluorescent absorption respectively. Most of the general remarks there referring to the relative importance of the two terms hold equally well for these results, and we will therefore pass on to consider the terms separately.

The Scattering Terms.

We shall consider the scattering terms first. As seen from the values in the second column of Table IV, the total scattering for the most favourable case (curve 1) is only about one-third of that predicted by the classical theory (*i.e.*, 6.64×10^{-25}). For others it is even less. But the fact that these values show a progressive decrease is of special interest. According to the classical theory the scattering coefficient should be independent of the wave-length of the radiation. Richtmeyer, Hewlett and others have shown that for short X-rays this conclusion breaks down. Here we have the same effect shown clearly, for the first time, for γ -rays. As the beam is hardened the scattering coefficient steadily diminishes.

The classico-quantum treatment of Compton predicts a diminution of the scattering coefficient (σ) with wave-length, according to the formula

$$\frac{\sigma}{\sigma_0} = \frac{1}{1 + 2\alpha}, \quad (4)$$

where

$$\sigma_0 = 6.64 \times 10^{-25}, \quad \alpha = 0.0242/\lambda.$$

Before comparing the experimental results with theory, a small correction should be made for the rays scattered within the cone of the primary beam. This is obtained by integrating the expression (10), p. 221, between 0° and 18° . Column II of Table V gives the experimental values, expressed as fractions of σ_0 , column III the correction, column IV the corrected values, and column V

the mean-effective wave-lengths deduced from column IV by application of Compton's equation (4).

Table V.

I. $n.$	II. Λ/σ_0	III. $\sigma_s(0, 18)$	IV. σ/σ_0	V. $\lambda_s(\text{\AA.U.})$
1	0.294	0.034	0.327	0.0236
2	0.281	0.034	0.315	0.0223
3	0.279	0.033	0.312	0.0219
4	0.266	0.032	0.298	0.0206
5	0.265	0.032	0.297	0.0205

The Fluorescent Absorption Terms :

As before we shall assume the validity of the λ^3 law for these high frequencies. Apart from the experimental evidence derived from the absorption of short X-rays, the theoretical basis of the law has been developed by Kramers* in a recent publication. We shall represent the values given in Column II of Table IV by

$$B = \beta \lambda^3,$$

where β has the same value as for X-rays shorter than the K limit. Taking Richtmeyer and Warburton's† latest value (2.24×10^{-2}) we at once get for the mean-effective wave-lengths (λ_m) the values given in column II of Table VI. For purposes of comparison the corresponding values, as deduced from the scattering terms, are reproduced in column III.

Table VI.—Mean Effective Wave-lengths (in $\text{\AA.U.}$).

I. $n.$	II. λ_m	III. λ_s
1	0.0227	0.0236
2	0.0216	0.0223
3	0.0203	0.0219
4	0.0190	0.0206
5	0.0185	0.0205

The first point to be noticed is that, within the somewhat narrow range of λ_m concerned, the Z^4 law holds well. It is, of course, possible that with extremely short waves the law is modified in some hitherto unknown way, but so far there is *definitely* no sign of such an effect.

* Kramers, 'Phil. Mag.,' vol. 46, p. 836 (1923).

† Richtmeyer and Warburton, 'Phys. Rev.,' vol. 22, p. 539 (1923).

It will be seen from Table VI that the estimates of mean-effective wave-lengths (λ_s) given by Compton's theory lie close to those deduced from the fluorescent absorption terms; but that they are somewhat larger. The scattering, according to this theory is, ignoring the higher powers, proportional to λ and λ_s will therefore be given by $\frac{\Sigma I_\lambda \lambda \delta \lambda}{\Sigma I_\lambda \delta \lambda}$. On the other hand, the fluorescent absorption being proportional to λ^3 the quantity λ_m will be given by the cube root of $\frac{\Sigma I_\lambda \lambda^3 \delta \lambda}{\Sigma I_\lambda \delta \lambda}$. We should therefore expect the calculated λ_s to be slightly larger than λ_m . Remembering that the observed difference is in the right direction, it is certainly remarkable that Compton's theory should give values agreeing so well with those deduced from the fluorescent absorption terms. If at any time the extension of λ^3 law to γ -ray frequencies could be experimentally justified, the agreement of Table VI should constitute strong evidence in favour of Compton's formula.

If the range of mean-effective wave-lengths had been wider, it would have been possible to throw some light on this point. But even for an absorption of the primary beam amounting to 92 per cent., λ_m is diminished by only 20 per cent. Remembering the wide range of wave-lengths of rays emitted by $\text{RaB} + \text{C}$, this is indeed one of the most unexpected and surprising results of these experiments. It leads us directly to a consideration of the spectral distribution of energy in the beam.

Spectral Distribution of Energy.

The *averaged* absorption coefficient of a complex beam depends both upon the wave-lengths of its constituents and their relative intensities; and, if the wave-lengths are known, it should be possible to obtain some idea of the intensity distribution.

For this purpose we shall *assume* five γ -rays whose energies and wave-lengths are given in columns II and III of Table VII. Since it so happens that γ_2 lies very close to the observed mean-effective wave-length, the preliminary calculations are simplified by replacing γ_1 and γ_2 by a ray (γ') of energy 4.5×10^5 volts and wave-length 0.0276 Å.U. On account of the uncertain amount of the characteristic radiation from heavy elements entering the ionisation chamber, the experimental results with Fe filters and Al absorbers only will be considered.

The calculations being somewhat long and tedious, only an outline of the

procedure and the final results will be given. The mass-absorption coefficients in Fe and Al of each of the four γ -rays are calculated according to the formula

$$\frac{\mu}{\rho} = \left\{ \frac{\sigma_0}{1+2\alpha} + \beta\lambda^3Z^3 \right\} \cdot \frac{Z}{A} \cdot N, \quad (5)$$

where the various symbols have the same significance as before. These values of μ/ρ are then individually corrected for scattering along the primary beam. Now, if I_K is the intensity of any γ -ray in the primary beam, its intensity on entering the ionisation chamber will be

$$I_K \cdot e^{-(\mu/\rho)_{Fe} \cdot m} \cdot e^{-(\mu/\rho)_{Al} \cdot m'}$$

where m, m' are the masses per unit area of the filter and the absorber respectively. The observed coefficient in Al with one filter — $(\mu/\rho)_{Al}$ of the entire beam will be given by

$$(\mu/\rho)_{Al} = \frac{\sum_{K=1,2,\dots} (\mu/\rho)_{Al} I_K \cdot e^{-(\mu/\rho)_{Fe} \cdot m} \cdot e^{-(\mu/\rho)_{Al} \cdot m}}{\sum_{K=1,2,\dots} I_K \cdot e^{-(\mu/\rho)_{Fe} \cdot m} \cdot e^{-(\mu/\rho)_{Al} \cdot m}} \quad (6)$$

where the summation on the right-hand side is carried out for all the rays. Similarly for the other two filters. By solving these three equations the intensities of the four rays may be expressed in terms of one of them. By ignoring the small absorption of $\gamma_3, \gamma_4, \gamma_5$, with 0.5 cm. Fe filter, we get the ratios $\gamma_1 : \gamma_2 :: 1 : 3.88$. We then finally arrive at the results given in column IV of Table VII (to the nearest half integer).

Table VII.

I. γ -Ray.	II. Energy in Volts.	III. Wave-length.	IV. Intensity Per Cent.
		Å.U.	
γ_1	0.300×10^6	0.0413	17.5
γ_2	0.600	0.0206	67.5
γ_3	0.900	0.0123	3.0
γ_4	1.400	0.0080	10.0
γ_5	1.900	0.0065	2.0

Discussion.

It can be shown, by considering the results of Richardson* and Moseley† together, that the soft constituents should possess about 25 per cent. of the energy of the beam. Remembering the difference in method, our value for γ_1 is in satisfactory agreement with their result.

* Richardson, 'Roy. Soc. Proc.,' A, vol. 91, p. 396 (1915).

† Moseley, 'Phil. Mag.,' vol. 23, p. 302 (1912).

As is known, Ellis* has made a visual estimate of the intensities of the homogeneous rays measured by him. If the γ -rays from RaC be divided into three broad groups, with mean wave-lengths at 0.0368, 0.0178 and 0.0084 Å.U. respectively, then, according to him, their relative intensities are in the ratio of 15 : 50 : 35. Thus again our value for γ_1 agrees very well with Ellis's estimate. It is also noteworthy that Ellis has recorded a strong line (of intensity 16 on his scale) at 0.0087 Å.U., *i.e.*, coinciding almost exactly with our γ_4 .

When we compare the total intensity of γ_3 , γ_4 and γ_5 relative to that of γ_2 , a serious discrepancy appears. Ellis's estimates make the ratio 35 : 50, while our results put it at 15 : 68. The difference is far outside the experimental error of either series of measurements, and the only *satisfactory* way of explaining it is to suppose that, like X-rays from a heavy anticathode, the emission of monochromatic γ -rays is accompanied by a considerable amount of white radiation. There is nothing in Ellis's work, which referred *only* to the intensities of the homogeneous rays, against this conclusion, which, in fact, is suggested by many theoretical considerations.

The general radiation, like the homogeneous rays, may have its origin in the nucleus itself, or, as Rosseland has suggested, it may represent the classically radiated energy of an accelerated β -particle shooting past the nucleus. In the latter case the mechanism will not be quite so simple, but similar to that indicated by Kramers† and Wentzel‡ in their explanation of continuous X-radiation. On the other hand, it may be due to a modification of the wave-lengths of the nuclear γ -rays through scattering by the extra-nuclear electrons, as suggested by Compton's theory. Such a process would result in a general spreading out of the line spectrum.

Allowing, then, for the existence of continuous γ -radiation, our results, taken in conjunction with Ellis's, indicate that a considerable fraction of the total γ -ray emission is in the form of general radiation, with a maximum at about 0.02 Å.U., upon which the homogeneous rays are superimposed. On this view the small variation in mean-effective wave-length, even for large absorption of the primary beam, becomes readily intelligible.

Scattering Results.

The intensities of the primary beam (I_0) and of the scattered beam entering the ionisation chamber (I_θ) are given in Tables VIII and IX. Position 1

* Ellis, *loc. cit.*

† Kramers, *loc. cit.*

‡ Wentzel, 'Zeit. f. Phys.,' vol. 27, p. 257 (1924).

refers to the case when the angle (ϕ) between the primary beam and the axis of the chamber was 40° , position 2 when it was 60° .

Table VIII.—Position 1. $\phi = 40^\circ$.

Element.	Source 1.			Source 2.			Mean $\times 10^3$.
	I_0 .	I_θ .	$I_\theta/I_0 \times 10^3$.	I_0 .	I_θ .	$I_\theta/I_0 \times 10^3$.	
Al	14,800	97	6.58	23,650	157	6.71	6.64
Cu	14,900	100	6.73	23,400	160	6.82	6.78
Sn	15,300	87	5.69	23,300	129	5.54	5.62
Pb	18,850	70	3.68	23,200	87	3.75	3.71

Table IX.—Position 2. $\phi = 60^\circ$.

Element.	Source 1.			Source 2.			Mean $\times 10^3$.
	I_0 .	I_θ .	$I_\theta/I_0 \times 10^3$.	I_0 .	I_θ .	$I_\theta/I_0 \times 10^3$.	
Al	26,300	62	2.32	33,750	80	2.40	2.36
Cu	25,550	60	2.37	33,250	75	2.25	2.31
Sn	25,400	45	1.78	29,050	50	1.70	1.75
Pb	23,200	22.4	1.02	28,150	30	1.06	1.04

Analysis of Scattering Results.

The scattered beam will be absorbed to different extents in the different radiators, and in order to obtain mutually comparable results, a correction must be applied. The magnitude of this correction, depending largely upon the angle of scattering, will vary uniformly from one end of the chamber to the other. It is difficult to evaluate it exactly, but to a first approximation the correction, as applied to the central ray, will be valid for all the rays in the cone.

Now Florance* and others have shown that if allowance is made for the absorption of the ray scattered at θ° , its intensity is given by

$$I_\theta = I_0 \frac{\sigma_\theta}{\mu' \sec \theta - \mu} [e^{-\mu d} - e^{-\mu' d \sec \theta}],$$

which gives

$$\frac{\sigma_\theta}{\rho} = \frac{1}{\rho} \cdot \frac{I_\theta}{I_0} \cdot K, \quad (7)$$

where

$$K = \frac{\mu' \sec \theta - \mu}{e^{-\mu d} - e^{-\mu' d \sec \theta}}.$$

* Florance, 'Phil. Mag.,' vol. 20, p. 921 (1910).

Here σ_θ/ρ is the mass-scattering coefficient in the direction θ , μ and μ' the absorption coefficients of the primary and the scattered beams respectively, and d the thickness of the radiator.

In order to evaluate K , the experimental values of μ were used, while those for μ' were calculated, assuming the wave-lengths of the scattered rays as given by Compton's theory, from the general absorption relation (5).

The values of σ_θ/ρ , as given by (7), are shown in columns III and VI of Table X, while the *scattering per electron* $(\sigma_\theta)_e$ calculated according to

$$(\sigma_\theta)_e = \frac{1}{N} \cdot \frac{A}{Z} \cdot \frac{\sigma_\theta}{\rho} \quad (8)$$

is shown in columns IV and VII. It will be seen that for elements of low atomic number, σ_θ/ρ remains approximately constant, but diminishes steadily with increasing Z . This agrees completely with the results of Florance and Gray. For each position of the chamber, however, the scattering per electron is seen to remain constant to within 3 per cent. This would be expected on any theory of scattering. It shows incidentally that under the experimental conditions the amount of characteristic radiation from heavy elements, entering the ionisation chamber, relative to that of the scattered rays is very small.

Table X.

I. Element.	Position 1.			Position 2.		
	II. Mean $I_\theta/I_0 \times 10^3$	III. $\sigma_\theta/\rho \times 10^3$	IV. $(\sigma_\theta)_e \times 10^{27}$	V. Mean $I_\theta/I_0 \times 10^3$	VI. $\sigma_\theta/\rho \times 10^3$	VII. $(\sigma_\theta)_e \times 10^{27}$
Al	6.64	1.73	5.97	2.36	0.729	2.51
Cu	6.78	1.70	6.14	2.31	0.736	2.66
Sn	5.62	1.58	6.21	1.75	0.652	2.55
Pb	3.71	1.41	5.85	1.04	0.645	2.70
Mean $(\sigma_\theta)_e = 6.04 \times 10^{-27}$						2.60×10^{-27}

Comparison with Theory.

For scattering in any direction the classical theory gives :—

$$I_\theta/I_0 = \frac{e^4}{2m^2c^4} (1 + \cos^2 \theta), \quad (9)$$

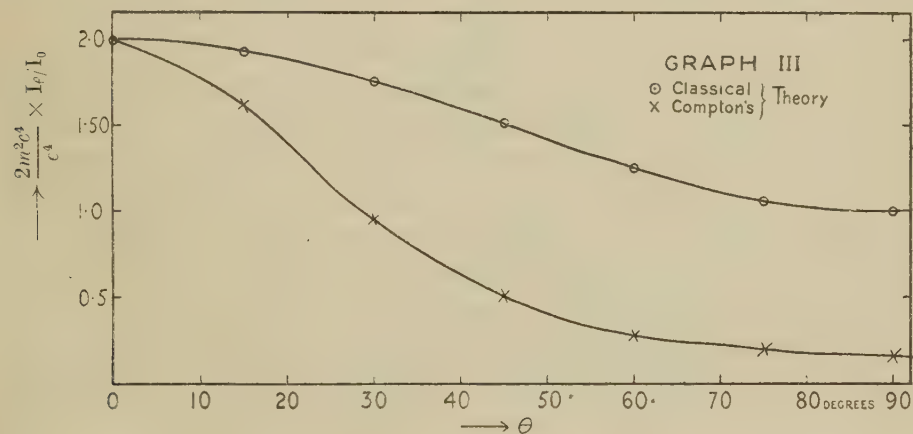
while Compton's theory gives

$$I_{\theta}/I_0 = \frac{e^4}{2m^2c^4} \left[\frac{1 + \cos^2 \theta + 2\alpha(1 + \alpha)(1 - \cos \theta)^2}{\{1 + \alpha(1 - \cos \theta)\}^5} \right], \quad (10)$$

where $\alpha = 0.0242/\lambda$.

In order to compare the experimental results with theory, the expressions for I_{θ} in (7) and (8) must be integrated over the face of the ionisation chamber. Now the integration between the limits assigned by experiment is unmanageable. The difficulty is overcome by using the following graphic method of solution, which, it is hoped, will yield values sufficiently accurate for our purpose.

Dividing the face of the ionisation chamber into small strips, each 1 cm. wide, the solid angles subtended by the individual strips at the centre of the radiator were calculated. It is assumed that the intensity of the scattered rays remains constant over each strip, and is equal to the value corresponding to its middle point. This value is read from Graph III, where



I_{θ}/I_0 , according to (9) and (10), is plotted against θ , λ being taken equal to $0.023 \text{ \AA.U.}$, *i.e.*, the value from absorption results. The intensity is multiplied by the corresponding solid angle, and the sum of the products represents the total intensity within the cone. This is corrected for the small absorption in the face of the ionisation chamber. The final values, both theoretical and experimental, are given side by side in Table XI.

Table XI.—Scattering per electron $(\sigma_e)_e$ for Two Positions of the Ionisation Chamber.

Position.	Theoretical.		Experimental.
	Classical.	Compton.	
I	1.82×10^{-26}	0.68×10^{-26}	0.60×10^{-26}
II	1.45×10^{-26}	0.29×10^{-26}	0.26×10^{-26}

It will be seen that the values given by the classical theory are three to five times those actually observed; while Compton's theory yields values which are, at least, of the right order of magnitude. These are about 12 per cent. too high. The difference, though certainly outside the experimental error, is not at all surprising when one remembers the simplifying devices that have been introduced in the calculations. For instance, the exact value of the solid angle, as given by

$$\omega = 2\pi(1 - \cos \phi),$$

is about 3 per cent. less than the sum of the values actually used. This factor alone should reduce the theoretical value in Table XI by about 3 per cent., but, on the other hand, some neglected factors may operate in the opposite direction. On the whole it may be concluded that while the classical theory completely breaks down, the Compton theory predicts values which are in reasonably good agreement with experiment.

If the scattered beam were a mixture of "truly" scattered and modified rays, its intensity should lie between the values given by the two theories. The fact that the observed values are even less than those given by Compton's theory strongly suggests that, unless the mean effective wave-length has been much overestimated, the scattered γ -rays are practically all modified. This is in agreement with an early conclusion of Compton* that the amount of truly scattered rays, for angles greater than 40° , is negligible.

Summary.

Extending the previous work of the writer, the absorption of γ -rays from $\text{RaB} + \text{C}$, "hardened" progressively with suitable filters, has been measured in four typical elements. A modified form of balance method was employed.

* Compton, 'Phil. Mag.', vol. 41, p. 770 (1920).

It is found that in every case the atomic absorption coefficient μ_a is closely expressed by a relation of the form

$$\mu_a = AZ + BZ^4,$$

where A and B are constants for a particular beam, but decrease steadily as the rays become harder. The two terms on the right-hand side represent scattering and fluorescent absorption respectively. The γ -rays, therefore, in their absorption by matter, obey the same general law as X-rays of much lower frequency.

The mean-effective wave-length of the beams, as deduced on Compton's theory from the scattering terms and on the λ^3 law from the fluorescent absorption terms, agree very well with one another.

The results indicate that the homogeneous γ -rays are superimposed upon a background of general radiation which contains a considerable fraction of the total γ -ray emission with a maximum at about 0.02 Å.U.

By means of a conical ionisation chamber, capable of revolving about the radiator, the intensities of the rays scattered within a definite cone have been measured for two positions of the chamber.

The classical theory predicts values which are three to five times those actually observed. There is, on the other hand, reasonably good agreement between the experimental values and those calculated on Compton's formula giving the angular distribution of the scattered rays.

The work was made possible, in part, by grants from the Office of the High Commissioner for India, and from Peterhouse, for which the writer is deeply indebted. My best thanks are due to Prof. Sir Ernest Rutherford for his kind interest and helpful discussion, and to Dr. E. C. Stoner for invaluable advice and help.

The Zeeman Effect in Strong Magnetic Fields.

By P. KAPITZA, Ph.D., and H. W. B. SKINNER, B.A.*

(Communicated by Prof. Sir E. Rutherford, O.M., F.R.S. Received July 25, 1925.)

[PLATES 4 AND 5.]

§ 1. *Introduction.*

From the time of Zeeman's discovery, the Zeeman effect has been the subject of a large amount of work; but hitherto experiments have been limited by the fields obtainable with an electro-magnet. It is known that the strongest field which can be obtained with the largest practicable electro-magnet is about 80,000 gauss. On account of the necessity in Zeeman effect experiments for uniformity of the field over a considerable volume, no experiments seem to have been performed in fields stronger than 40 or 50,000 gauss.

In a recent paper† a method has been described by which considerably stronger fields may be produced. The general principle is to obtain the field by passing a large current through a coil (without iron) for a very short time; so that the coil has no time to heat up. The current is produced by short-circuiting a specially constructed accumulator battery through the coil, and in this way it is possible to use a power of 1,000 k.w. A field of strength up to 500 k.g. may be obtained in a very small volume; but for the study of the Zeeman effect, it has only been found possible to use fields of strength up to 130,000 gauss,‡ since we must have the field uniform over a reasonable volume in which to place our source of light.

Since the duration of the field is only about $1/300$ th sec., and fields are not accurately repeatable, the method of performing the experiments on the Zeeman effect must be carried out in a different way from that ordinarily used. The source of light must be such as to produce a fully exposed spectrum in $1/300$ th sec. For the source of light we have used a spark from a large condenser battery, and owing to its large luminosity a quartz spectrograph was employed. This, on account of the strength of the fields, gave sufficient resolving power for observation of the Zeeman effect. Further, it is essential to produce the

* Senior 1851 Student and Coutts Trotter Student of Trinity College, Cambridge.

† P. Kapitza, 'Roy. Soc. Proc.,' A, vol. 105, p. 691 (1924); 'Roy. Soc. Proc.,' A, vol. 106, p. 602 (1924).

‡ A preliminary note on these experiments on the Zeeman Effect in Strong Magnetic Fields was given in a letter to 'Nature' (vol. 114, p. 273, 1924).

spark at the moment when the field reaches its constant maximum value, and for this purpose special timing arrangements must be used.

We shall not enter into the details of the production of the field, for they are described in the papers quoted. The discussion of the details of the spark will be given in a subsequent paragraph.

§ 2. General Description of Apparatus.

The general arrangement of the apparatus is shown in fig. 1. The accumulator battery (1), the main switch (2) and the oscillograph arrangement (3)

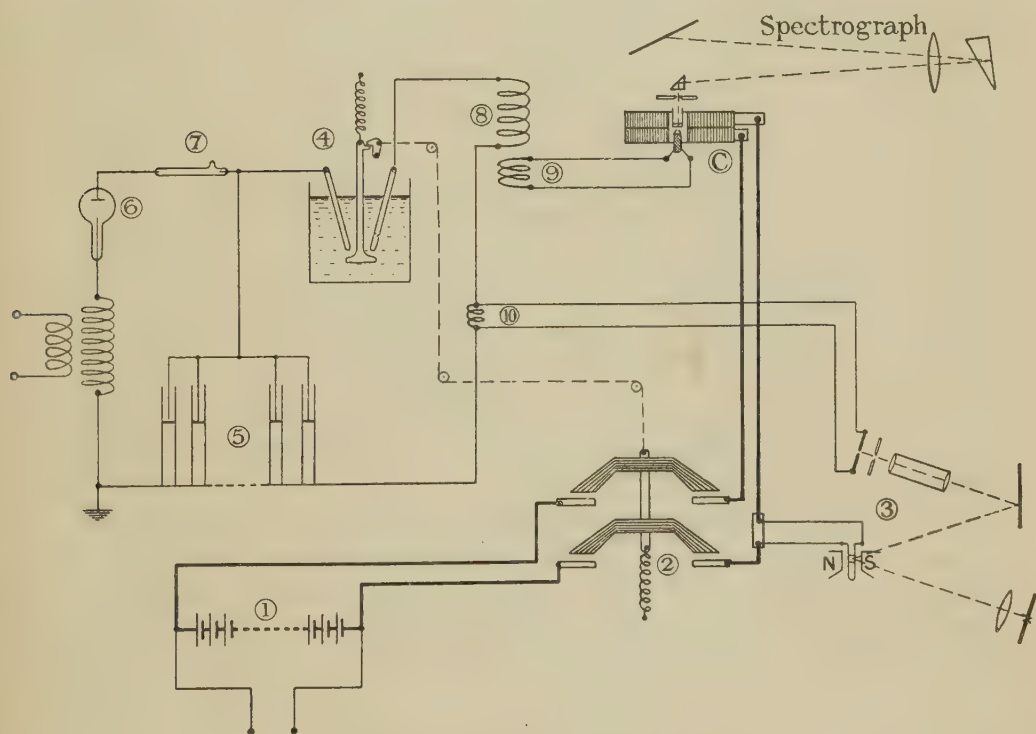


FIG. 1.

are the same as described in the previously quoted papers. At the time of the present experiments the accumulators were showing signs of wear, and gave less power than previously. The magnet coil (C) was specially made for this experiment and will be described later. The main switch (2) suddenly connects the coil for 1/100th sec. to the battery, and a current of about 3,000 amps. passes. The same switch in falling operates, by means of a Bowden cable and trigger release, an oil-immersed high-tension switch (4) which dis-

charges the condensers (5), so producing the spark within the magnet coil. The condensers* are of Moscicki type and have a capacity of 1/10th mfd. They were charged to about 30,000 volts by means of an induction coil rectified by a Kenotron valve (6), water resistances (7) being interposed to avoid oscillations and consequent over-tension during charging. The condensers were not used to produce the spark directly, but were discharged through a coil (8), coupled to a coil of fewer turns (9), in such a way as to make a transformer. The terminals of coil (9) were connected to the spark gap, inside the magnet coil. This transformer arrangement was convenient for several reasons. In the first place, the high-tension leads are kept away from the magnet coil. Secondly, the transformer stepped-down the voltage considerably, thus producing a more localized and brighter spark. And further, by altering the number of turns of coil 8 and the coupling of transformer, the intensity and duration of the spark was subject to control. The necessity for this will be discussed in §3.

In order to time the moment of production of the spark with the occurrence of the field, a small auto-transformer (10) was placed in the condenser discharge circuit. In the secondary of this a small spark gap is placed, and a spark from this throws a beam of light on to the falling plate of the oscillograph on which the current is recorded. Since this small spark occurs simultaneously with the main spark, the oscillogram shows at once whether or not the timing is correct. (An example of an oscillogram is shown in fig. 4, Plate 4.) Adjustment of the timing could be made by a screw-control of the trigger release of the high-tension switch (4).

In making an experiment, the condensers were first charged. The release of the main switch (2) produces the field, and operates the spark, thus photographing the spectrum. The main switch is released by the falling plate of the oscillograph, which records the current in the coil. Thus the whole experiment is operated by the release of the falling plate.

§ 3. *The Spark and the Coil.*

The circuit as described in § 2 gave a spark with a frequency of 1,500 per second, and the damping was such that about five full periods were observed. Thus the length of time during which the spark lasted was about 1/300th sec. The frequency and duration of the spark were measured in a separate experiment by photographing it on a moving film. When all the coils are in action the breaking voltage of the spark is about 1,000 to 2,000 volts, and the

* We are much indebted to the Marconi Company for the loan of these condensers.

current, as estimated from the measured frequency of oscillation, of the order of 1,000 amperes.

We have worked with an air spark. It would probably be better, from the point of view of sharpness of the spectrum, to use a high vacuum spark. The smallness of the region in which the magnetic field is produced, however, makes this technically very difficult.

It has been found to be advantageous to increase the duration of the spark to as great a value as possible in order to obtain sharp lines in the spectrum. From the point of view of the intensity of the spectrum it does not matter whether the circuit is adjusted so that the spark lasts 1/1000th sec. or 1/300th sec. When the spark is not enclosed in the coil in which the field is produced, it makes no appreciable difference to the sharpness of the lines either. But when the spark is enclosed in the small volume within the magnet coil, in which the magnetic field is uniform, a marked improvement is produced in the spectrum obtained, the longer the duration of the spark.

This is what would be expected on the probable assumption that it is the pressure effect, and not any intrinsic effect of the large current, or high voltage, to which the broadening of the lines is due. A high pressure arises in the kernel of the spark, especially when this is formed in an enclosed space. Before this pressure has time to release itself the spark is over, and the spectrum obtained is the spectrum of materials under a high pressure. An increase in the time of duration of the spark naturally minimises this effect.

This shows that in order to obtain sharp lines it is necessary, besides increasing to a maximum the duration of the spark, to provide as large an outlet as possible for the vapour to be formed. The breadth of the line obtained on a photographic plate is in favourable circumstances about $0.5 \text{ \AA.U.}$

This brings us to the consideration of the actual arrangements used for the production of the spark. Two arrangements could be used for the production of a low-tension spark.

(1) A wire of suitable size connected between the electrodes which is blown by the current.

(2) Two electrodes very near together or even touching.

The latter was found to be better; it is more convenient to work, and the blowing wire tends to produce too much vapour. The choice of electrodes is a matter of some importance. Thick electrodes tend to produce too weak a spark, because too little vapour is produced. We found the use of pointed metal strip about 1/5th mm. in thickness the most satisfactory.

The strip was placed in the arrangement shown in fig. 2. The two strips

are separated by an ebonite plug P, which slips into an ebonite tube Q. The spark occurs at S, between the two pieces of strip. Where they project from the plug the strips are cut down to about $\frac{1}{2}$ mm. in breadth, and are bent over so as just to touch one another. The spark causes the evaporation of these projecting pieces.

In fig. 2 is shown the coil used for the investigation of the longitudinal effect with the sparking arrangements in position.

At the other end of the coil a quartz window W is introduced as shown. This is a small disc of quartz $2\frac{1}{2}$ mm. in diameter, and its function is to keep

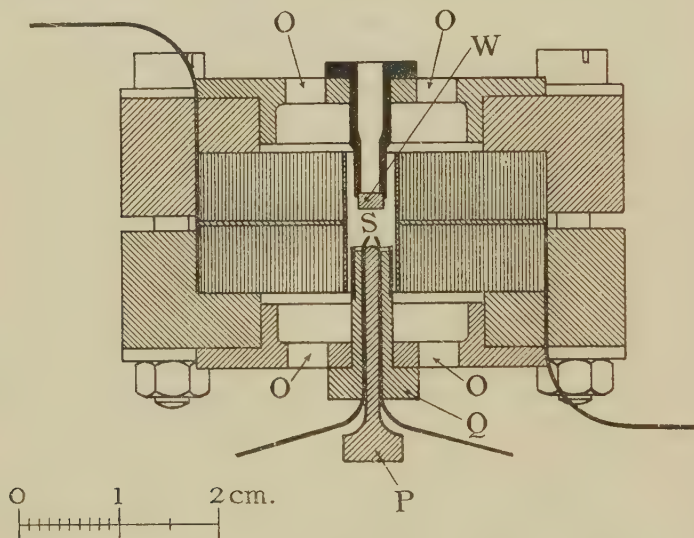


FIG. 2.

the part of the spark which is used in forming the spectrum within the uniform part of the field. Round the window and round the sparking arrangement the vapour can escape into the atmosphere through the holes O.

For the transverse effect the coil used was similar, except that it was necessary to have a gap to allow the light to pass out perpendicular to the lines of force. This gap also served for the escape of the vapour.

The magnet coil was wound of 60 turns of copper strip with silk and shellac insulation. Its construction was calculated in the way described in the papers previously referred to. The coil could be made smaller in size in our case, since a rise in temperature to about 120° did not matter. Also the coil was wound with strip whose cross-section increased outwards from the centre in

steps. Owing to these two factors the coil was rather more efficient than those described previously.

An attempt was made to increase the efficiency of the coil still further by cooling the coil in liquid air before allowing the current from the accumulator battery to pass through it. In this way it was hoped to obtain fields of about 250,000 gauss, instead of the maximum of 130,000 gauss which we could obtain with a coil of atmospheric temperature. Such fields were obtained; but it was found impossible to use them. The difficulty is that when the current begins to pass the coil is heated up, and the gases absorbed at liquid-air temperature are liberated suddenly. This causes a violent wind which invariably blows out the spark used as the source of light.

With the sparking arrangements described above, we have not had much trouble through the sparks being blown out by the magnetic field. At the moment of sparking, the force on the projecting ends at S is large, and they straighten themselves out parallel to the plug. But the spark gap is already broken and the spark still continues provided the thickness of the plug is not too large. It has been actually found that if this is the case, a spark of brief duration is the result, and if the electrodes are examined afterwards they are seen to be aligned parallel to the plug.

For the material of the electrodes, we have used the metals copper, aluminium and zinc, and magnesium. The spectra of the elements are obtained in some cases as emission and in others as absorption lines; but there are also usually lines due to impurities. The strongest of these impurity spectra are the spark spectra of magnesium and calcium. The lines of these spectra are sharp, and we have worked considerably with them. For example, the 1st Principal Doublet of Mg II, as obtained with Mg electrodes, is heavily reversed and rather broad. With electrodes of "pure" copper fine sharp emission lines are obtained. The 1st Principal Singlet of Mg I with Mg electrodes is extremely broadened; with Cu electrodes, again, it is frequently found either as a sharp absorption or sharp emission line according to circumstances.

Some of the electrode lines, however, were sharp enough for use. If electrode lines are required they may be obtained sharply at the sacrifice of the weaker "impurity" lines.

The fact that the impurity lines are sharp suggests that sharp lines will also be obtained if impurities are added. This was easily done by putting a little of a salt of the element required, in the form of the solution, on the electrodes. The function of the electrodes may thus be simply to hold the elements required. Between 5,000 and 3,000 Å.U. zinc is the best electrode to use, since

it shows very few lines and no continuous spectrum. Below 3,000 aluminium is the best, but it has the disadvantage of entering into chemical combination with quartz and of so spoiling the surface of the quartz window that a fresh one is required every time. For this reason copper was generally employed in this region.

In this way most of the first lines of the spectral series can be obtained with sufficient intensity in one flash. The second lines of the series are too faint to work with, since only a single flash can be given in the magnetic field. Since the exposure possible is limited, the use of a spectrograph which will pass a large amount of light is essential. We are much indebted to Prof. A. Fowler, F.R.S., for advising us, in the initial stages of the experiments, as to the kind of spectrograph which would be best suited for the work. A fairly high dispersion and large luminosity are the main essentials. We have used a Hilger E_1 quartz prism spectrograph. This can be used as far into the ultra-violet as 2,000 Å.U. Its dispersion varies from 17 Å.U. to the mm. at 5,000 Å.U. to 2.5 Å.U. to the mm. at 2,400 Å.U.

The use of the fastest photographic plates is necessary, and we have used the Ilford Iso-Zenith plate (H and D 700), which is sensitive from 2,400 to 5,100 Å.U., and has proved satisfactory.

The spectrograph was used without condensing lens. Owing to the small size of the quartz window it was found that the use of a condensing lens did not improve the sharpness of the spectrum, and the adjustments were more easily made without it. The source was so placed that the prism of the spectrograph was filled with light.

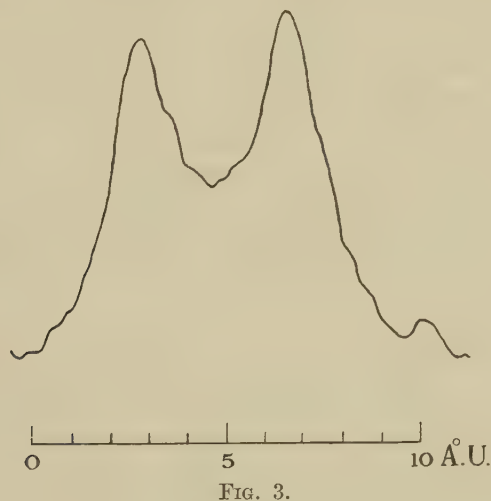
The magnet coil was rigidly supported on a table, the height of which could be adjusted, in front of the slit of the spectrograph. The alignment of the hole in the magnet coil on the slit of the spectrograph was performed by removing the spark plug P (fig. 2) from the coil, and shining an arc, kept in a standard position at a distance through the coil, on to the slit.

Three spectra were usually taken on the same plate—a comparison spectrum, taken without any magnetic field, in the centre, and two spectra in the magnetic field near it on either side.

§ 4. *The Measurement of the Separations and of the Field Strength.*

The measurement of the Zeeman separations was originally carried out, usually using a Hilger comparator. The measurements, however, left something to be desired for consistency. Measurements could not be repeated very accurately, so that the limits of error were rather high.

We therefore carried out a series of photometric measurements of the plates, using a photometer similar to those designed by Koch* and Dobson.† The instrument is not a recording photometer and, for the present purpose, it was sufficient to take readings on the electrometer scale, the plate being usually moved through $1/200$ th mm. between readings. A slit of $1/50$ th mm. was used, since a narrower slit only served to bring out kinks due to the grain of the emulsion. In this way a photometer curve was drawn for the doublet whose separation was required, and the doublet separation was found as the distance between the maxima. The separation of the Zeeman doublets, namely, from 0.15 to 0.3 mm., could be obtained in the case of the best lines to within about 0.005 mm. and the error could be estimated from the shape of the peaks. It was found that separations of a given doublet could be repeated to within this order of accuracy. One of the photometer curves, namely, of the Hg line 4047 in a field of 106,000 gauss, is reproduced as an illustration in fig. 3.



Actually, the accuracy with which the doublets could be measured varied considerably in different cases; so, in all the measurements which are to be given, it has been necessary to state the probable errors of measurement.

The photometric measurements were found to be far more satisfactory than the visual measurements. On the whole, the photometric measurements give slightly less values for the separations than the visual measurements. It might perhaps be expected that the tendency of the photometric measurements

* 'Ann. der Phys.,' vol. 39, p. 705 (1912).

† 'Roy. Soc. Proc.,' A, vol. 104, p. 248 (1923).

will be to underestimate the doublet separations owing to the lack of complete separation of the components. This will tend to bring the maxima, between which measurements are made, nearer together. In most cases, however, the separation was sufficiently complete for this difference to be small. It is, on the other hand, difficult to say what effect the lack of separation will have on the visual measurements, since one's visual idea of a doublet does not seem to correspond very closely with the photometric curves. For this reason also the photometric measurements are to be preferred, and it is these measurements which are given when there is any question of numerical agreement.

In order to determine the field, the current which passed through the magnet coil in any actual experiment was measured from the oscillogram (an example of which is given in Plate 4). The oscillograms also showed that during the time of the spark, the current in the coil did not vary from its mean value by more than $\frac{1}{2}$ per cent. To deduce the field a knowledge of the magnetic constant of the field is required, and this was determined in the following way. A small single-layer solenoid was wound on a glass tube, ground to a cylindrical shape with an accuracy of 0.005 mm. Its diameter was 2.325 mm. and its length about 10 cm. This was suspended on a balance, and hung axially through the magnet coil. The magnetic constant was deduced from a determination of the force exerted on the solenoid when known steady currents are passed through the solenoid and the magnet coil. The total estimated error in the field determination is about 1 per cent., which was sufficient for the present experiments.

§ 5. *General Description of Results.*

Some six-times enlarged examples of portions of our spectra are given in figs. 5 to 7, Plates 4 and 5. In these, dark lines indicate emission lines.

The total separations in a field of 120,000 gauss range mostly from 0.3 mm. to 0.15 mm. on the original plates, according to the wave-length of the line involved and its particular splitting. The maximum separation in wave-length observed is 5.8 Å.U. in the case of the Zn line λ 4680.

For the most part, the lines in the longitudinal effect appear in the field as split into two components. Sometimes the sharpness of the components is equal to that of the unaffected line, showing that a simple type of splitting is taking place; but sometimes it is not. This indicates that there are two or more components inseparable with the resolving power available. In individual cases separations into four lines in the longitudinal effect have been observed.

In some cases the Zeeman splitting, as seen from the plates, appears not to occur exactly about the position of the unaffected line. A slight shift to the red is sometimes observed. The shift is, however, not regular in magnitude when the conditions are repeated, and for this reason it appears to be of secondary origin. Probably it is a pressure shift, due to the action of the magnetic field in affecting the geometrical character of the spark. This explanation is supported by the fact that the shifts were found when using sparks of short duration (1/1000th sec.) as the source of light. When the duration of the spark was increased to the maximum possible value (1/300th sec.) they no longer appeared.

We have observed some cases of the appearance of lines in the field which are faint, or absent when there is no field. The lines in question are, however, lines whose series relationships are at present unknown. It is possible that these cases are examples of the effect found by Paschen and Back on the appearance of "forbidden" components in a magnetic field.

In what follows we shall be concerned exclusively with lines of a simple spectral type, since these afford the best material for a test of the extension of the ordinary observed relationships of the Zeeman effect in fields of strength up to 130,000 gauss.

§ 6. *Results.*

We first consider results on the longitudinal Zeeman effect of lines for which the occurrence of the Paschen-Back effect is not evident. The most accurately measurable of these lines are those which show a simple type of splitting into two components only in the longitudinal effect. Such lines are Singlets which have been found in fields such as are ordinarily used for the investigation of the Zeeman effect to show a normal Zeeman effect; the $s-p_2$ components of Principal or Sharp doublets, which have been found to show a splitting three times the normal splitting; and the $s-p_3$ components of Principal or Sharp triplets, which show a twice-normal splitting. Of these, the larger separation found in the case of the triplet lines makes the measurements more accurate, and we shall discuss these first. Our method of analysis is to calculate a value for the estimated field from each measured Zeeman separation by assuming the splitting factor found in fields of ordinary magnitude, and to compare the Estimated Field with the Measured Field.

In Table I are given the results in the case of the $s-p_3$ components of the sharp triplets of Zn and Hg, λ 4680 and 4047. The corresponding magnetic fields are arranged in descending order of magnitude. Examples of the splitting of these lines are given in Plates 4 and 5.

Table I.—Triplet Lines (p_3 -s).

Spectrum No.	Element.	λ	Estimated field kilogauss.	Measured field kilogauss.	Excess of estimate over measured field, per cent.	Total probable error, per cent.
57	Zn	4680	140.7 $\pm$ 2	127.5 $\pm$ 1	10.6	2.3
58	Zn	4680	140.0 $\pm$ 2	126.8 $\pm$ 1	10.4	2.3
112	Zn	4680	115.0 $\pm$ 2	106.1 $\pm$ 1	8.4	2.8
112	Hg	4047	115.0 $\pm$ 1.5	106.1 $\pm$ 1	8.4	2.4
116	Zn	4680	109.9 $\pm$ 5	103.8 $\pm$ 1	5.9	7.8
116	Hg	4047	107.7 $\pm$ 3	103.8 $\pm$ 1	3.8	3.9
124	Hg	4047	88.0 $\pm$ 5	89.6 $\pm$ 1	— 1.8	6.7
123	Zn	4680	89.9 $\pm$ 3	88.0 $\pm$ 1	2.2	4.6
110	Zn	4680	73.6 $\pm$ 4	76.3 $\pm$ 1	— 3.7	6.6
120	Zn	4680	67.8 $\pm$ 3	68.4 $\pm$ 1	— 1.0	5.7

It is seen immediately that, roughly, the assumed splitting factor (namely, 2.0) for the lines is correct. However, in the higher fields, the splitting appears to be distinctly greater than is given by this factor. The result in the highest fields is 10 per cent. greater, and this is outside the limits of error of the experiments. In the lower fields (though unfortunately the errors are here greater owing to the smaller separation of the components) the splitting agrees with the theoretical value; and, moreover, the occurrence seems to be high enough to exclude a value 10 per cent., such as we find in the case of the strongest fields. Hence we conclude that between the field strengths 70,000 and 130,000 gauss, the separation is not a linear function of the field strength, but increases more rapidly than the field strength.

We shall leave the discussion of this point for the moment, and turn to consider the case of the Doublet and Singlet lines, which are given in Tables II and III.

Table II.—Doublets (s - p_2).

Spectrum No.	Element.	λ	Estimated Field (K.G.).	Measured Field (K.G.).
57	Ca II	3968	127 $\pm$ 10	127.5 $\pm$ 1
57	Al I	3944	135 $\pm$ 7	127.5 $\pm$ 1
58	Ca II	3968	127 $\pm$ 7	126.8 $\pm$ 1
69	Mg II	2802	108 $\pm$ 5	110.5 $\pm$ 1
112	Ca II	3968	110 $\pm$ 2	106.1 $\pm$ 1
112	Sr II	4215	112 $\pm$ 5	106.1 $\pm$ 1
85	Mg II	2802	102 $\pm$ 8	97.5 $\pm$ 1
123	Ca II	3968	80 $\pm$ 10	88.0 $\pm$ 1
123	Sr II	4215	83 $\pm$ 5	88.0 $\pm$ 1

Table III.—Singlets (S-P).

Spectrum.	Element.	λ	Estimated Field (K.G.).	Measured Field.
52	Mg	2852	122 ± 7	126.1 ± 1
112	Ca	4227	109 ± 10	106.1 ± 1

Here we see that an approximate agreement with the theoretical values is obtained for all field strengths up to 130,000 gauss. It will be seen, however, that, as is to be expected, the limits of error of measurement are greater in this case, and it is not possible to state that a high value of the splitting factor, such as we obtained in the case of the triplets, is definitely excluded. All that can be stated is that the measurements, as far as they go, show no signs of such an effect. The fact that, in a few cases, we have on the same plate both doublet lines, which seem to show approximately the splitting which might be expected, and triplet lines, which show the large splitting, gives further confidence in the reality of the anomalous effect on triplets, since it makes the results to some extent independent of the measurement of the field strength.

We have next to consider the case of the $s-p_1$ components of doublets and the $s-p_2$ components of triplets. We have a measured case of the latter, which theoretically splits into components ± 1.5 , $\pm 2\Delta\nu_n$. This is the line 4357 of Hg. It shows no signs of the separation of the individual Zeeman components, only two components being seen. The estimated field, calculated on the basis of a splitting factor 1.75, is 113 ± 5 in a measured field of 106.1 K. gauss; so that this line may possibly also show the high splitting characteristic of the $s-p_3$ components of the triplets.

In the doublets, the state of affairs is much more complicated. To the eye, the splitting appears to be simple, only two rather broadened Zeeman components being seen. The theoretical separation between individual components $\pm \frac{3}{2} \pm \frac{5}{2}$ is rather greater than in the case of the Hg line 4357, and this greater separation shows itself in the appearance of slight double maxima in the photometric curves. These maxima are usually not at all symmetrical in intensity, and are not sufficiently distinct to make useful measurement possible.

We now pass on to consider our results on the Transverse Zeeman Effect. It should be stated at once that these are not very complete. Measurement is difficult owing to the number of the components. Also the necessary hole in the side of the magnet coil reduces its efficiency considerably, so that the

highest field strength cannot be reached. The results are sufficient to show that extra components are being brought in in the Transverse Effect ; and that the magnitude of the separations is roughly what would be expected. Further, a plate taken, using a Nicol prism to cut out, first, the $\perp$ components, then the $\parallel$ components, showed qualitatively that, in the case of the doublet of Ca II, λ 3933, 3968, the polarizations are also as would be expected.

We may further mention a few results obtained on the spectrum of Al II. In a letter to 'Nature,'* Russell has given a series scheme of these singlets. We have observed the splitting of some of the lines he mentions. One of them is the line λ 3900, which he gives as 3P-3D, and which was found by Paschen† to show the normal Zeeman effect. This we have confirmed. Another line is λ 3057. This is given by Russell as 3S-3 p_2 , in which case it should show a 3/2 normal splitting. We have found that its splitting factor is decidedly higher, namely, about 1.8, instead of 1.5. Again, the line 3050.1 given by Russell as 4P-4S, should show a normal effect. It has a simple splitting with a factor of about 1.5, indicating probably that λ 3050.1 and not λ 3057 is the combination line 3S-3 p_2 .

The splitting of a considerable number of other lines has been observed, but the method at present gives hardly sufficient detailed information to serve as a guide in spectrum analysis, although it may serve as a check.

§ 7. Cases of the Paschen-Back Effect.

The method of strong fields may be expected to give examples of the Paschen-Back effect, and we now mention some of those observed.

(a) Ca II diffuse doublet λ 3159, 3179, 3181.

This case is shown in fig. 7, Plate 5. The line 3181 does not appear in the field though lines of equal strength can be seen. This is a case of an incomplete partial Paschen-Back effect, the expected splitting in the field in question being comparable with the d -term separation.

(b) Mg pp' group, λ 2783.0, 2781.5, 2779.8, 2778.3, 2776.8.

We are dealing here with six pp' combinations, two of which happen to coincide. There are therefore five lines observed. In weak fields, these lines all show a 3/2 normal splitting. In the longitudinal effect in a magnetic field of about 120,000 gauss, six components appear, and the positions of these are susceptible to comparatively small changes in the field strength. The effect observed is probably an intermediate stage of the Paschen-Back effect.

* Vol. 113, p. 163.

† 'Ann. der Phys.,' vol. 71, p. 537 (1923).

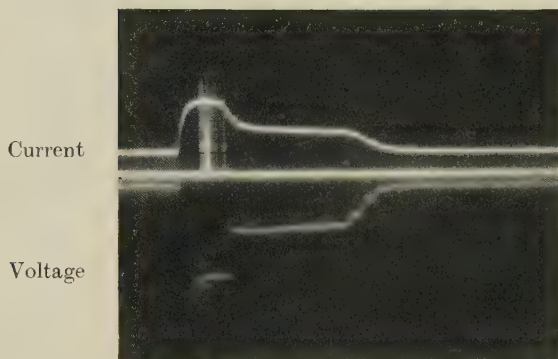


FIG. 4.

Current 2,880 amps. Field 110,500 gauss.

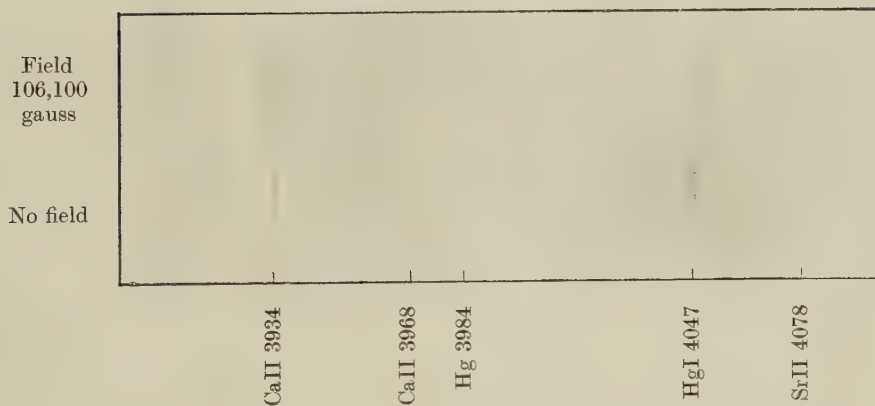


FIG. 5.

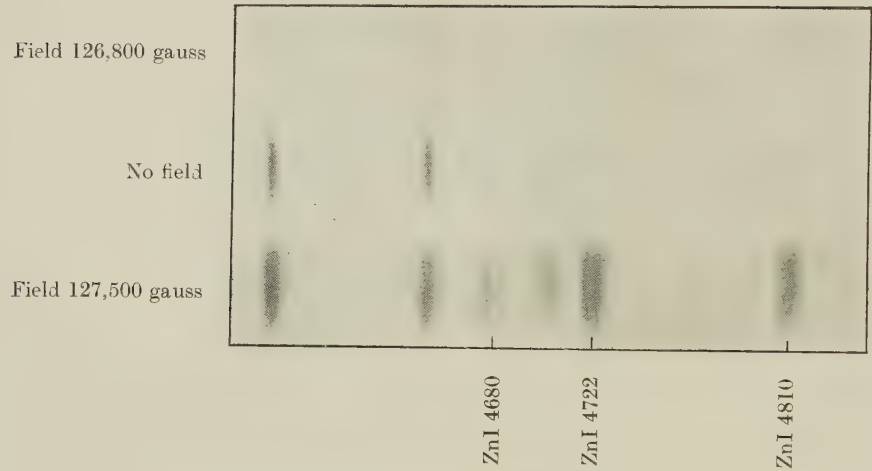


FIG. 6.

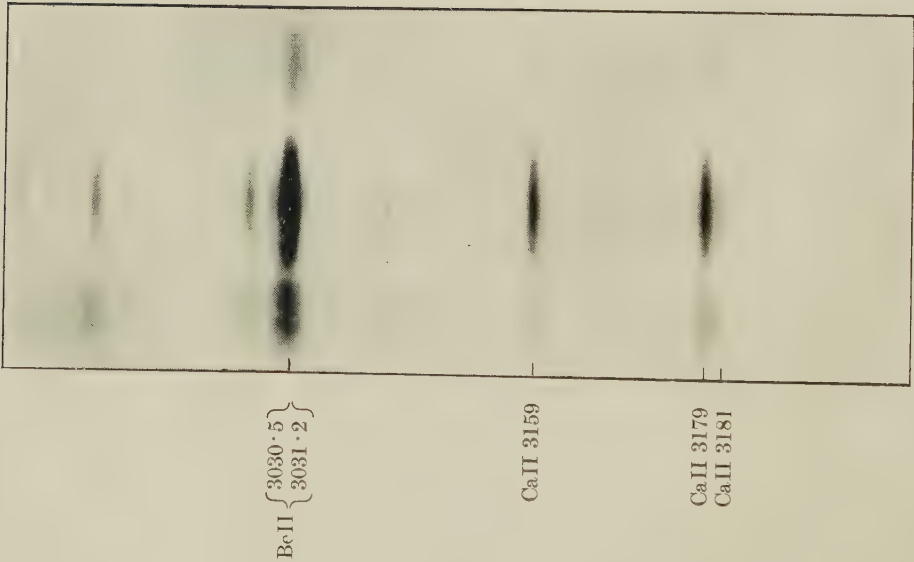


FIG. 7.

(c) Be pp' group. λ 2650·88, 2650·81, 2650·75, 2650·72, 2650·66, 2650·57.

This is a group consisting of six extremely close lines which are, of course, not separated with the resolving power available. In the field the group is found to split into two sharp components, while in the transverse effect the appearance of a central component is proved by the fact that merely a general broadening of the line is observed. Measurements give for the splitting factor in a field of 110,500 gauss the value 0·98. Thus the splitting is normal, and we have a case of the complete Paschen-Back effect.

§ 8. Discussion of Results.

We have seen that our experiments indicate that in fields of strength between 70,000 and 130,000 gauss, the splitting factors of some of the lines seem to be only roughly the same as those obtained in fields of strength up to 40,000 gauss. In the case of the triplet p_3 - s lines of Zn and Hg, there appears to be a systematic increase in the splitting factors as the field is increased from 70 to 130,000 gauss. Further, though the accuracy of the experiments is there less, no signs of this effect were obtained in the case of the doublet s - p_2 lines of Mg II, Ca II, Sr II and Al, or in the singlet S-P combination of Mg I and Ca I.

The question at once arises whether this anomalous splitting can be due to a Paschen-Back effect. The fact that the splitting factors obtained for the Zn and Hg lines agree, however, makes this apparently impossible, since the multiplet splittings of the Hg and Zn triplets in a new field are in the ratio of about 10 to 1. Further, a comparison with known data shows that the separations of the Zn and Hg triplets are too great for any such effect to be anticipated. Also, we are indebted to Dr. W. Heisenberg for the remark that the p_3 -term does not split at all in a magnetic field. The splitting of the p_3 - s line is therefore controlled by the splitting of the s -term, and this, being single, cannot show any Paschen-Back effect. For these reasons it would seem that the explanation of the effect as a Paschen-Back effect is excluded.

It seems unprofitable to speculate very deeply into the origin of the large splitting of the Zn and Hg lines at the present moment, because the range of field strength over which the effect has been observed is too small for a systematic study. Also, the theory of the Zeeman effect is at present largely formal. The following remarks may, however, be of some interest.

According to the formal analysis of Landé, the splitting of a turn in a magnetic field is determined by a precession frequency gO_H , where O_H is the

Larmor rotation frequency and g is a constant for a particular type of turn. In order to interpret the observed effect we should have to suppose that either O_H/H or g is a function of H .

Taking the first alternative, the presence of the terms of the Larmor theorem, which depend on the square of O_H would give an effect of the type observed ; but calculation shows that these would not be expected to be appreciable in fields of less than 10^6 or 10^7 gauss.

If we suppose g to be a function of H , we must base considerations on the Zeeman effect model, consisting of a series electron and an atom core, which are both subject to precessions in a magnetic field, and which, in addition, influence one another. Heisenberg* has shown that with certain important assumptions, the correct g -values may be obtained from this model. It would seem that the only loophole for an explanation of the observed effect is in the interaction term between the core and the series electron ; this conceivably might depend on the field strength.

That this kind of explanation is perhaps the correct one is possibly supported by the fact that it is in the triplet spectra that the anomalous splitting in high fields is observed. In double spectra, we have to suppose that the core consists of closed groups. In triplet spectra, however, the core is alkali-like, and consists of a set of closed groups with one electron left over. In the former case the interaction of the core with the series electron might be expected to be simple ; but in the case of the triplets it is possible to suppose that the interaction may be of a more detailed character.

Summary.

(1) A method of utilising the transient magnetic fields (up to 130,000 gauss) produced by accumulator discharges through a coil, which have been described previously by one of us, for the study of the Zeeman effect, is given. The method of measuring the fields is also described.

(2) The method involves photographing a spectrum with an exposure of not more than $1/300$ th sec., and a means for doing this, using a high dispersion quartz spectrograph, is also given. It consists of a special application of a large condenser battery to give a single localized spark.

(3) The method used to time the spark with the moment of the occurrence of the field is described.

(4) The results of photometric measurement of the Zeeman separations indicate that the splitting is approximately what would be expected from the

* 'Zs. f. Phys.,' vol. 26, p. 291 (1924).

usual experiments on the Zeeman effect, if the Zeeman separations are proportional to the field strength. But with the triplet p - s combinations of Zn and Hg, evidence is given that the splitting is not strictly proportional to the field strength between fields of 70,000 and 130,000 gauss. The splitting is 10 per cent. greater than would be expected in a field of 130,000 gauss. The splitting of the s - p combinations in doublet and singlet spectra seems to be normal. A suggestion for a possible interpretation of these facts is given.

(5) Some observed cases of the Paschen-Back effect are discussed.

The experiments have been performed with the continuous co-operation of Mr. E. J. Laurmann, to whom we wish to express our thanks. We should also like to express our gratitude to Prof. Sir Ernest Rutherford, O.M., F.R.S., for his constant interest in the work.

Structure in the Secondary Hydrogen Spectrum.—Part III.

By O. W. RICHARDSON, F.R.S., Yarrow Research Professor of the
Royal Society.

(Received July 9th, 1925.)

In previous papers it has been shown that a considerable number of the lines of this spectrum can be arranged in series by starting from the lines which are selectively weakened in the electron discharges, which have been described by Prof. Tanaka and the writer.* In some parts of the spectrum this process has reduced the number of lines of any strength which are not arranged in series very considerably, so that it seemed possible that some regularity might be becoming apparent among the remaining lines which are not selectively affected in those discharges. The present communication deals mainly with the progress which has been made up to the present along these lines, but it also includes some results which have been obtained by the former method.

The 24 lines in Table I can be arranged as a strong band with P, Q and R branches. The lines give combinations and the numerical properties are quite remarkable.

* Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 106, p. 640 (1924).

Table I.—157 PQR.

Series No. 157 P (*m*).

	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
<i>m</i> .	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
1								6035.02	16565.38 (0)		
2			++					6107.86	16367.81 (1)	- 197.57	+ 16.52
3			++					6176.18	1 P (7) 16186.76 (3)	- 181.05	+ 54.60
4		++	-			F 1, 3		6224.81	16060.31 (9)	- 126.45	+ 63.88
5								6249.15	15997.74 (3)	- 62.57	+ 69.05
6			+	O				6246.63	16004.22 (2)	+ 6.48	+ 65.82
7								6218.53	16076.52 (0)	+ 72.30	+ 60.11
8								6167.64	16208.93 (3)	+ 132.41	

Series No. 157 Q (*m*).

1			+	O				5956.42	†16783.96 (3)		
2		+		+				5947.27	16809.80 (6)	25.84	49.75
3		++		+				5920.65	16885.39 (6)	75.59	64.84
4		++	++					5871.81	†17025.82 (4)	140.43	66.99
5			++	++				5801.14	159 R(5) 17233.24 (3)	207.42	68.43
6			++					5709.74	157 R(2) 17509.09 (2)	275.85	61.97
7				++				5601.66	17846.91 (0)	337.82	54.79
8		+						5481.08	E ₃ II 18239.52 (4)	392.61	

Series No. 157 R (*m*).

0			++					5891.31	16969.45 (1)		
1			+					5803.93	17224.96 (1)	255.51	28.62
2			++					5709.74	157 Q (6) 17509.09 (2)	284.13	57.77
3			+	++				5600.38	†17850.99 (3)	341.90	67.25
4		+						5474.89	E ₁ E ₃ 18260.14 (1)	409.15	68.60
5	+			++				5335.30	18737.89 (0)	477.75	64.37
6								5185.28 (T)	19280.01 (<i>p</i> , <i>d</i>)	542.12	57.64
7								5028.84	†19879.77 (1)	599.76	

I, II, III denote weakened E₁, E₂, E₃ enhanced in 1st, 2nd and 3rd type discharges respectively here and throughout the tables.

† Absent at - 252° C. (McLennan and Shrum).

‡ denotes an unresolved doublet (M and B).

There are several lines claimed by other series. 157 P (3), 16186·76 (3) is also claimed as 1 P (7), for which, however, it is much too strong. 16060·31 is a strong Fulcher line and is much too strong for 157 P (4). 157 P (5), 15997·74 is claimed by Allen as a Fulcher line, and the claim is admitted by Curtis.* In the Q series 157 Q (5), 17233·24 is also claimed as 159 R (5), but it seems to have enough strength for both this and 157 Q (5). 17509·09 has to function both as 157 Q (6) and 157 R (2). Its strength seems about normal for 157 R (2), but a much weaker line would do for 157 Q (6). The only weakened line is 18239·52 assigned to 157 Q (8). This is weakened in the second-type discharge, but it is also recorded as enhanced in the third type. 157 R (4), 18260·14 is recorded as enhanced in the first and third types.

The second differences vary over a wide range of values, but the variations are systematic within a reasonable margin of error. This is particularly true of the R series, which is most free from interference with lines claimed by other series. In fact, the second differences are a very similar function of the quantum numbers for all three series, as is shown by the graphs in fig. 1. The variation

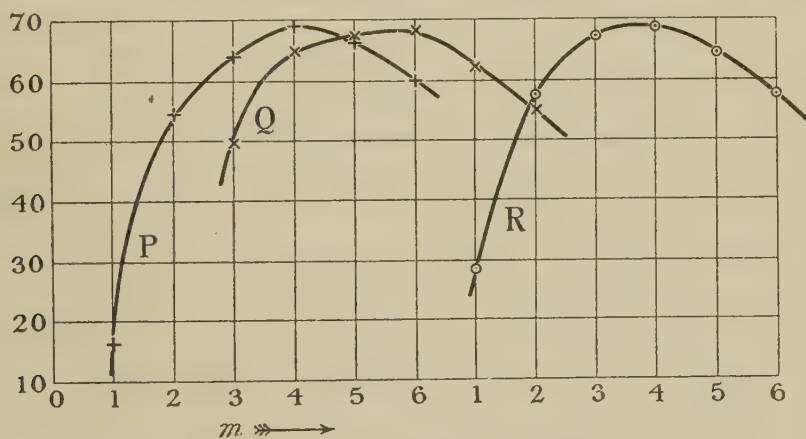


FIG. 1.—Second Differences in Series.

in the second differences appears to be of the same type as that already observed in 1 P, 28 Q, 201 R and other bands, but relatively much exaggerated.

There is a very close parallelism between the intensities of corresponding lines of the series of this band, as is shown in the following table, where Merton and Barratt's intensities, or Tanaka's, are given for the three series with the lines in juxtaposition:—

* Curtis, 'Roy. Soc. Proc.,' A, vol. 107, p. 574 (1925).

Table II.

m for P and Q $\longrightarrow$	1	2	3	4	5	6	7	8
Int. of P (m)	0	1	3	9*	3	2	0	3
Int. of Q (m)	3	6	6	4	3	2	0	4
Int. of R ($m - 1$)	1	1	2	3	1	0	p	1

Table III.—Initial Term Data for 157 PQR.

m .	$R(m) - Q(m)$.	$Q(m + 1) - P(m + 1)$.	Diff.	Term Diff.	Means.	2nd Diff.
0		218.58		$F(1) - F(0)$	218.58	
1	441.00	441.99	-0.99	$F(2) - F(1)$	441.50	$\left. \begin{array}{l} 222.92 \\ 257.46 \end{array} \right\}$
2	699.29	698.63	$+0.66$	$F(3) - F(2)$	698.96	$\left. \begin{array}{l} 266.59 \\ 269.36 \end{array} \right\}$
3	965.60	965.51	$+0.09$	$F(4) - F(3)$	965.55	$\left. \begin{array}{l} 269.85 \\ 265.90 \end{array} \right\}$
4	1234.32	1235.50	-1.18	$F(5) - F(4)$	1234.91	$\left. \begin{array}{l} 261.07 \end{array} \right\}$
5	1504.65	1504.87	-0.22	$F(6) - F(5)$	1504.76	
6	1770.92	1770.39	$+0.53$	$F(7) - F(6)$	1770.66	
7	2032.86	2030.59	$+2.27$	$F(8) - F(7)$	2031.73	

Table IV.—Final Term Data for 157 PQR.

m .	$R(m) - Q(m - 1)$.	$Q(m) - P(m + 1)$.	Diff.	Term Diff.	Means.	2nd Diff.
0	185.49			$f(1) - f(0)$	185.49	
1	415.16	416.15	-0.99	$f(2) - f(1)$	415.66	$\left. \begin{array}{l} 230.17 \\ 207.71 \end{array} \right\}$
2	623.70	623.04	$+0.66$	$f(3) - f(2)$	623.37	$\left. \begin{array}{l} 201.76 \\ 202.36 \end{array} \right\}$
3	825.17	825.08	$+0.09$	$f(4) - f(3)$	825.13	$\left. \begin{array}{l} 201.42 \\ 203.93 \end{array} \right\}$
4	1026.90	1028.08	-1.18	$f(5) - f(4)$	1027.49	$\left. \begin{array}{l} 206.28 \end{array} \right\}$
5	1228.80	1229.02	-0.22	$f(6) - f(5)$	1228.91	
6	1433.10	1432.57	$+0.53$	$f(7) - f(6)$	1432.84	
7	1640.25	1637.98	$+2.27$	$f(8) - f(7)$	1639.12	

The second differences in the term numbers are very far from constant, and the course of these functions is shown in fig. 2. The behaviour of the initial terms is like that of both terms of 1 P, 28 Q, 201 R, but much exaggerated, and consists of a sharp rise to a maximum, followed by a falling off at a gradually

* Most of this is a strong Fulcher line.

accelerating rate as the value of m increases. The behaviour of the final terms is similar, but in the opposite sense, that is to say, a sharp diminution followed by a slow rise at an accelerating rate. This wide variation in the second difference, and the uncertainty of its origin, makes the detailed interpretation of this band difficult. If we assume that the equation $F(m) = B(m - P)^2$ can be applied over the range of m from 0 to 2 as a first approximation, though obviously a very rough one, we should have $F(1) - F(0) = B \times (1 - 2P) = 218.58$ and $2B = 222.92$. To satisfy this $P = -\frac{1}{2}$, at any rate to this approximation. This makes the initial states of $\frac{1}{2}$ quantum type with P

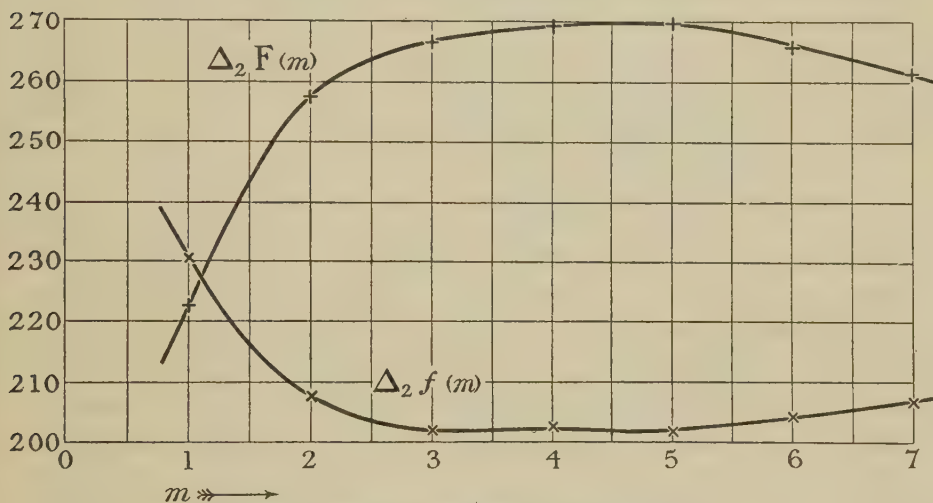


FIG. 2.—Second Differences in Term Numbers.

negative. Making similar assumptions as to the final terms, we get $f(1) - f(0) = b(1 - 2\rho) = 185.49$ and $2b = 230.17$, which require $\rho = -0.306$. These might also, if the matter were more fully understood, be $\frac{1}{2}$ quantum states with ρ negative. This position is not very strong, but it is supported by the non-existence of the line $Q(0) = P(1) - Q(1) + R(0)$. If the values of $F(1)$ and $f(1)$ calculated from the above values of B, b, P and ρ are used in conjunction with $Q(1)$, the value of ν_0 is found to be 16732.8 , which is, no doubt, only a very rough guess at the magnitude of this quantity. The value of the moments of inertia, which apparently are variable with m , are rather low, and are consistent with the distribution of intensity among the lines in each series.

The arrangements immediately following would appear to be isolated branches in the red and yellow part of the spectrum.

Table V.—Series No. 153 P (*m*).

<i>m.</i>	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
1			++	O				5893·95 Ki (6)*	16961·86 (3)		
2	++		+	++	Z			I, II, III 5982·54†152 R (1)	16710·70 (8)	251·16	46·19
3	++		++		Z			Im, II, III _m 6090·92 83 Q (1)	16413·35 (7)	297·35	47·74
4	+							6221·73	‡16068·26 (4)	345·09	47·11
5								6377·39	15676·06 (2)	392·20	

* Denotes an unresolved doublet (M. & B.).

† Weakened at -252°C. (McL. & S.).

‡ Absent at -252°C.

If there are any lines beyond $m = 5$ they are in the insensitive extreme red or infra-red, and are beyond the limit of Merton and Barratt's tables. 16961·86 is also claimed as Kiuti's Q (6), but it is given by Merton and Barratt as an unresolved doublet, and in any event is far too strong for $m = 6$ in Kiuti's series. 16710·78 is also claimed as 152 R (1). This line is not essential to 152 R (m), but it seems rather strong for 153 P (2). 16413·35 is also claimed by 83 Q (1), but the assignation of this line to 83 Q (m) has already been noted as doubtful. In any case, there is enough strength in it for both positions. The two strongest lines—153 P (2) and 153 P (3)—are both weakened in each type of discharge.

The second differences of 153 P (m) are rather variable. In order to see whether this might be due to an error in the measurement of one or more of the lines, Mr. W. E. Williams re-measured these lines for me on one of Prof. Merton's plates, with the following results :—

Table VI.

<i>m.</i>	→	1.	2.	3.	4.	5.
Williams' value of wave number in vacuo	→	16961·85	16710·60	16413·32	16068·29	15676·05
1st Difference	→		251·25	297·28	345·03	392·24
2nd Difference	→			46·03	47·75	47·21

As will be seen, the re-measurements make very little difference, but, if anything, the disparity between the second differences is accentuated. It may be that this is a series with almost constant second differences to which the line 16961·85 does not belong. On the whole, the distribution of intensity among the lines seems to agree better with the probable moment of inertia if this line is included.

If we assume that these lines are a whole quantum series with the enumeration given in Table V, using the equation $P(m) = \nu_0 - (2m - 1)Ca + m^2Cd$, we obtain from the first three lines only, $Ca = 90\cdot94$, $Ce = 114\cdot04$, $Cd = -23\cdot10$ and $\nu_0 = 17075\cdot90$. If we assume it is a half quantum series with the equation $P^{\frac{1}{2}}(m) = \nu_0 + \frac{1}{4}Cd - m(Ca + Ce) + m^2Cd$ and the same enumeration, we get $Ca = 79\cdot39$, $Ce = 102\cdot49$, $Cd = -23\cdot10$ and $\nu_0 = 17172\cdot10$. In any event, ν_0 is quite near the ν_0 s for Fulcher's 1st Band, Kiuti's series and series No. 3 $P(m)$. One possible Ce (114·04) is identical with Ca for the combination 59 $Q(m)$, 56 $R(m)$, (114·06).^{*} Other possible values of Ca and Ce are not far from those for 81 $R(m)$. Different estimations of all these quantities would, of course, be obtained if the line 16961·86 = 153 $P(1)$ were dropped.

The next series, 156 $Q(m)$, has variable second differences, but the variations are quite systematic, as is seen by their plot against m in fig. 3. The last line,

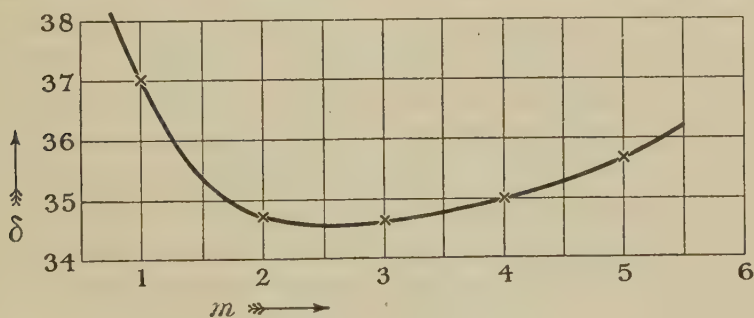


FIG. 3.—156 $Q(m)$.

16897·97, is also claimed by 159 $R(3)$, but it is given by Merton and Barratt as an unresolved doublet. It is much too strong here, and no doubt most of the strength belongs to 159 $R(3)$. This is the only line which is certainly weakened in the I-III type discharges.

^{*} Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 107, p. 609 (1925).

Table VII.—Series No. 156 Q (*m*).

<i>m</i> .	Properties.							W.L. in Air		Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)					
1								5712·19	E ₂ (?)	17501·57 (0)		
2			++	+				5716·00		*17489·91 (3)	11·66	37·03
3	++		++	O				5731·92		17441·22 (7)	48·69	34·73
4	+		++					5759·51	I ? II ?	17357·80 (4)	83·42	34·64
5			++	O				5798·95		17239·74 (3)	118·06	34·99
6			—					5850·89	159 R (8)	17086·69 (2)	153·05	35·67
7	++		++	+				5916·24	I, II, III 159 R (3)†	16897·97 (6)	188·72	

* Absent at — 252° C. (McL. & S.).

† Unresolved doublet (M. & B.).

The line 17086·69 here attributed to 156 Q (6) is also claimed by a second line of the same series, namely, 159 R (8). However, it has enough strength to cover both positions. Whether the line 17357·80 = 156 Q (4) is weakened in the I and II type discharges is doubtful. In the records of the weakened lines prepared by the writer and Prof. Tanaka there is a weakened line recorded as 17355·21 (4) which has been assigned to 152 R (4). It seems most likely that this is the weakened line, but a re-examination of the plates shows that these lines are not sufficiently distinct, and it is just possible that the weakened line is 17357·80. The line 17501·57 (0) is in our list of lines enhanced in the second type discharge, but for similar reasons, as in the case just preceding, it is not absolutely excluded that the enhanced line may not be 17498·18 (4).

If we put as an approximation $F(m) = B(m - P)^2$ and $f(m) = b(m - \rho)^2$, then we get from the three lines 156 Q (1) Q (2) Q (3), using the enumeration in Table VII, $2(B - b) \approx 37$ and $2(BP - b\rho) \approx 44$. These can only be satisfied with reasonable values of B and b provided both P and ρ are near unity. As an illustration, if $P = 1$ and $\rho = 0.9$ we should have $b = 70$ and $B = 88.5$, values which are not unreasonable in view of the distribution of intensity among the lines. If we use these values in the terms involving P^2 and ρ^2 in $Q(1) = \nu_0 + B(1 - P)^2 - b(1 - \rho)^2$ we obtain without any additional ambiguity $\nu_0 = 17495$. — The nearest ν_0 known to this is that of 1P, 28Q, 201R at 17307·43. The requirements of this paragraph could, of course, equally well be met by depressing all the *ms* in Table VII by unity and giving to P and ρ values near zero.

Table VIII.—Series No. 158 R (*m*).

<i>m</i> .	Properties.							W.L. in Air.		Wave Number (Int.).	1st Diff.	2nd Diff.	3rd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)		<i>I</i> <i>m</i> , <i>II</i> <i>m</i> , <i>III</i> <i>m</i>				
1	++							6174·03	3P (3)	16192·42 (6)			
2	++							6067·70	I II 3P (2)	16476·14 (5)	283·72		
3	+		+	++	Z			5963·46		16764·15 (5)	288·01	4·29	0·88
4			++					5861·56		17055·59 (3)	291·44	3·43	2·25
5			++					5762·70	201 R (7)	17348·19 (2)	292·60	1·16	2·06
6			++	++				5667·40		†17639·89 (0)	291·70	-0·90	
			Mis sing										
8								5490·1—		18209·6— [*]			
9				++				5407·03		18491·16 [—]	281·56		

[*] This is a very faint line measured by Tanaka.

† Absent at -252° C. (McL. & S.).

The two weakened lines 16192·42 and 16476·14 are both claimed by 3 P (*m*). 16192·42 is probably too strong in 3 P (*m*), but 16476·14 hardly so. It is difficult at the present stage to adjudicate between the relative claims of 3 P (*m*) and 158 R (*m*) for these two lines. 17348·19 assigned here as 158 R (5) is also claimed, perhaps rather doubtfully, as 201 R (7). It seems, if anything, rather strong in both series.

If 158 R (*m*) is a real series, the initial and final moments of inertia are nearly equal and, in fact, their differences are only comparable with the differences in the moments of inertia in either state caused by changes in the rotational quantum numbers. For the lowest values of *m* the final moment of inertia exceeds the initial; as *m* increases the disparity diminishes and becomes zero between *m* = 4 and *m* = 5. If the doubtful lines *m* = 8 and *m* = 9 really belong here, the initial moment of inertia exceeds the final value for high values of *m*. If we use only the three first lines and apply $R(m) = \nu_0 + (2m - 1)Ce + m^2 Cd$, $Ca = 140\cdot79$, $Ce = 138\cdot64$, $Cd = 2\cdot15$ and $\nu_0 = 16051\cdot63$. Applying $R'(m) = \nu_0 + \frac{1}{4}Cd + m(Ca + Ce) + m^2 Cd$ to the same lines, $Ca = 139\cdot72$, $Ce = 137\cdot57$, $Cd = 2\cdot15$ and $\nu_0 = 15912\cdot45$. The value of Ca 140·79 is identical with the value of B (140·91) for 202P, 110Q, 101R,* and, in fact, owing to the smallness of *Cd* all the values of both *Ca* and *Ce* are quite close

* Richardson and Tanaka, *loc. cit.*

to this. $\nu_0 = 16051\cdot63$ is very close to ν_0 ($16058\cdot19$) for the doubtful sequence $4R(m)$, whilst $\nu_0 = 15912\cdot45$ is not far from $\nu_0 = 15961\cdot9$ — for $159R$, $159Q^*$.

Table IX.—Series No. 154 Q (*m*).

<i>m</i> .	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.	3rd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)					
1		++						5949·90*	186 R (1) 16802·38 (9)			
2		++	+					5924·82	*16873·41 (7)	71·03	116·30	
3		++						5859·79	17060·74 (3)	187·33	116·30	0·00
4	+		++					5757·33	17364·37 (3)	303·63	117·81	1·51
5			+	+				5620·90	II 170 Q (1) 17785·81 (2)	421·44	118·37	0·56
6			+					5455·33	18325·62 (0)	539·81	118·91	0·54
7				O				5266·04	18984·34 (6)	658·72		

* Enhanced at 252° C. (McL. and S.)

The first line, 16802·38, is also claimed as the first line of $186R(m)$ and may possibly not belong here. The line 17785·81 is also required as $170Q(1)$, where, however, it is probably too strong. Except for this line, none of the lines of this series have been recorded as weakened. The second differences increase a little with increasing *m*, but the rate of increase, as shown by the third differences, is not quite uniform. A re-measurement of the line 17060·74 by Mr. Williams gave the value 17060·69. If this value is used, the successive third differences become 0·15, 1·36, 0·61 and 0·54. The third differences are a continuous function of *m*, within the limits of observational error, and are not really large considering the large value of the second difference for this series.

If we treat this series like $156Q(m)$ ante, assuming $F(m) = B(m - P)^2$ and $f(m) = b(m - \rho)^2$ as provisional approximations, and if all the lines are included with the numeration in Table IX, we get from the first three lines $2(B - b) = 116\cdot30$ and $2(BP - b\rho) = 103\cdot42$. Since $B - b$ is large B must also be large, and to satisfy these equations P must be in the neighbourhood of unity. Probably the same is true of ρ , but it is not certain, as b may be rather small. In the equation $Q(1) = \nu_0 + B - b - 2(BP - b\rho) + BP^2 - b\rho^2$ everything is now determined except $BP^2 - b\rho^2$. If for the

* Richardson, ‘Roy. Soc. Proc.’ A, vol. 109, p. 35. Part II.

purpose of guessing at this term, we assume, arbitrarily and as an approximation,* that $P = \rho$, we obtain $P = \rho = 1 - \frac{1}{9}$ and $BP^2 - b\rho^2 = 45.97$, which leads to $\nu_0 = 16801.68$.

If we reject the first line in Table IX and reduce the value of m for each of the others by unity, we obtain $B - b = 58.15$ and $BP - b\rho = -6.44$. This requires a value of P in the neighbourhood of zero, but the magnitude of ρ is not so certain, as b might be rather small. If for the purpose of estimating the term $BP^2 - b\rho^2$ we make the arbitrary assumption* that $P = \rho$, we find $P = \rho = -\frac{1}{9}$ and $BP^2 - b\rho^2 = 0.72$, compared with $B - b = 58.15$ and $2BP - 2b\rho = -12.88$. These values give $\nu_0 = 16801.66$, which is identical with the value got by making similar assumptions when the first line was included. The same result is got if we make the extreme assumption $b = 0$. Another extreme assumption is $P = 0$. This gives $b\rho = 6.44$, and as the smallest known value of either B or b is $b = 31$ for 202P 104Q 58R, this requires, with some probability if not with certainty, that $\rho \gtrsim$ about $\frac{1}{4}$ or $b\rho^2 \gtrsim 1.6$. If this value of $b\rho^2$ were used in $Q(1) = \nu_0 + B - b = 2(BP - b\rho) + BP^2 - b\rho^2$, we should obtain $\nu_0 = 16804$. In point of fact, the intensity distribution for the lines of 154 Q (m) suggests a high value of b as well as of B ; so that, on the assumption $P = 0$, $b\rho^2$ is likely to be much less than 1.6. It seems that no plausible assumptions can remove ν_0 far from 16802.

Table X.—Series 186 R (m).

m .	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
1		++						5949.90	*154 Q (1)	16802.38 (9)	
2		++	++					5822.80	†17169.12 (5)	366.74	10.96
3			++	++				5697.46	17546.82 (3)	377.70	11.41
4								5573.86	*†17935.93 (1)	389.11	10.29
5			++	O				5452.54	18335.33 (0)	399.40	

* Enhanced at -252°C .

† Probably a doublet (W. E. Williams).

‡ Much enhanced at -252°C . (McL. & S.).

* These assumptions are, perhaps, not altogether arbitrary. They can, at any rate, be defended on the empirical ground that out of the 15 combinations so far published the widest difference is $P = \frac{3}{4}$ and $\rho = 1$, for the doubtful combination 159 R, 159 Q. The widest other difference is less than 0.2, and in many cases P and ρ are identical to the accuracy with which they can be determined by the available formulæ.

The first line, 16802·38, is claimed also as 154 Q (1), but, as we have seen, it could be abandoned in 154 Q (m) without any considerable detriment to that series. The line 17935·93 = 186 R (4) has been examined by Mr. W. E. Williams, who finds signs of duplicity in it. There are no weakened or strengthened lines in this series. There are, however, three lines enhanced and none weakened at -252° C. This is the only known series with so many enhanced and no weakened lines at -252° C., except Fulcher's S_3 and Σ_3 series.

If, however, we apply $R(m) = \nu_0 + (2m - 1)Ce + m^2Cd$, with the numeration shown in Table X, using the first three lines we get $Ca = 180\cdot63$, $Ce = 175\cdot15$, $Cd = 5\cdot48$ and $\nu_0 = 16621\cdot75$. Applying $R'(m) = \nu_0 + \frac{1}{4}Cd + m(Ca + Ce) + m^2Cd$ to the same three lines, we get $Ca = 177\cdot89$, $Ce = 172\cdot41$, $Cd = 5\cdot48$ and $\nu_0 = 16445\cdot23$. These values for Ca and Ce are almost identical with the corresponding quantities either for the initial or final states of the combinations 162P 169Q 163R, 161P 169Q 164R, 171P 170Q 162R, 163P 170·1Q 164R* and 84 PQR† and of the series 152R‡ and 11R'‡.

The series which follow are all in the extreme violet part of the spectrum.

The band 177 PQR (Table XI) is a fragment in which there are no known weakened or strengthened lines. The line 26331·73 = 177 P (6) is too strong, but it is also claimed as 183 R (2) (see below). Similarly 26591·22 = 177 P (5) is claimed as 181 R (4), but this is a weak line with no strength to spare, and its allocation to the present band may, perhaps, be considered doubtful. With the exception of these two lines and the very faint line 28135·41 attributed to 177 R (2), all the remaining lines are weak low-pressure lines.

Of the two possible combinations presented by this fragment, one has an error of $-0\cdot10$ and the other $+2\cdot25$. This error is large, but hardly sufficient to reject the combination principle, as the errors of measurement may be considerable for these lines. In any event, even if the combination principle does not apply exactly, the term numbers got by assuming it to apply may be approximately correct. These are given in Tables XII and XIII.

The second differences of the term numbers fall slowly as m increases. Assuming as a first approximation $F(m) = B(1 - P)^2$, and using only $B(3 - 2P) = 204\cdot58$ and $2B = 305\cdot42$, we find $B = 152\cdot71$, $P = 0\cdot8302$ and $F(1) = B(1 - P)^2 = 4\cdot40_2$. Similarly from $b(3 - 2\rho) = 194\cdot51$ and $2b = 297\cdot02$ we obtain $b = 148\cdot51$, $\rho = 0\cdot8451$ and $f(1) = b(1 - \rho)^2 = 3\cdot564$.

* Richardson, 'Roy. Soc. Proc.,' A, vol. 108, p. 553 (1925).

† Richardson, 'Roy. Soc. Proc.,' A, vol. 109, p. 35. Part II.

‡ Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 107, p. 602 (1925).

Table XI.—Series 177 P (*m*).

<i>m</i> .	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
3		+						3684·38	27133·88 (2)	275·48	8·30
4		+						3722·18	26858·40 (0)		
5								3759·57	181 R (4) 26591·22 (<i>g</i>)	267·18	7·69
6								3796·63	183 R (1) 26331·73 (2)	259·49	

Series 177 Q (*m*).

1		+						3620·14	27615·39 (0)	10·07	8·40
2		+						3618·82	27625·46 (0)		
3		+						3616·41	27643·93 (0)	18·47	8·23
4		+						3612·92	27670·63 (0)	26·70	

Series 177 R (*m*).

1		+						3593·52	27819·97 (0)	315·44	7·56
2								3553·23	28135·41 (<i>r</i>)		
3		+						3512·90	28458·41 (0)	323·00	

Table XII.—Initial Term Data for 177 PQR.

<i>m</i> .	R (<i>m</i>)—Q (<i>m</i>).	Q (<i>M</i> +1)—P (<i>m</i> +1).	Diff.	Term Diff.	Means.	2nd Diff.
1	204·58	—	—	F (2) — F (1)	204·58	305·42
2	509·95	510·05	—0·10	F (3) — F (2)	510·00	
3	814·48	812·23	+2·25	F (4) — F (3)	813·36	303·36

Table XIII.—Final Term Data for 177 PQR.

<i>m</i> .	R (<i>m</i>) — Q (<i>m</i> + 1).	Q (<i>m</i>) — P (<i>m</i> + 1).	Diff.	Term Diff.	Means.	2nd Diff.
1	194·51	—	—	<i>f</i> (2) — <i>f</i> (1)	194·51	297·02
2	491·48	491·58	—0·10	<i>f</i> (3) — <i>f</i> (2)	491·53	
3	787·78	785·53	+2·25	<i>f</i> (4) — <i>f</i> (3)	786·66	295·13
4	—	1079·41	—	<i>f</i> (5) — <i>f</i> (4)	1079·41	292·75

From $\nu_0 = Q(1) - F(1) + f(1)$ these values give $\nu_0 = 27614.55$. The value of B is practically the same as C_e for Fulcher's first band, b for 202 P, 110 Q, 101 R, and C_e for 38 R, and the value of b is the same as that of C_e for 27 P'. A number of other series have values of the corresponding constants which are not very far from these, and which might possibly be found to agree with them when more is known about this spectrum.

The next band, 180 PQR, consists of a Q series having five members and what appear to be fragments of associated P and R series. All the lines which are recorded in Merton and Barratt's tables are enhanced in one or other of the electron discharges, and the remaining very faint lines have not been investigated from this point of view. Two of the stronger lines have been recorded as low-pressure lines. As a matter of fact, this band was found by starting from the list of enhanced lines in the electron discharges prepared by the writer and Prof. Tanaka, and it uses all the enhanced lines which we recorded in this particular part of the spectrum.

Table XIV.—Series No. 180 P (*m*).

<i>m</i> .	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
3								3963.77	*25221.38 (<i>qd</i>)	262.99 269.35	6.36
4		++						4005.54	E ₂ 24958.39 (1)		
5								4049.24	24689.04 (<i>p</i>)		

* Not completely resolved from λ 3963.17 (Tanaka).

Series No. 180 Q (*m*).

1		++					S	3884.21	E ₁ E ₃	25738.04 (0)	13.57 18.85	5.28
2								3886.26	E ₂ E ₃	†25724.47 (0)		
3							S	3889.15	E ₁	*25705.62 (3)	25.81	6.96
4								3893.01		25679.81 (<i>q</i>)	33.79	7.98
5								3898.14		†25646.02 (<i>p</i>)		

* Not resolved from H₂ (M. and B). † Not completely resolved from λ 3897.66 (Tanaka).
‡ Measured on one plate only (M. and B).

Series No. 180 R (*m*).

2								3814.62	26207.51 (<i>r</i>)	220.81
3								3782.75	26428.32 (<i>p</i>)	

E₁, E₂, and E₃ denote enhanced in 1st, 2nd and 3rd type discharges respectively.

The term data are given in Tables XV and XVI.

Table XV.—Initial Term Data of 180 PQR.

m .	$R(m) - Q(m)$.	$Q(m+1) - P(m+1)$.	Diff.	Term Diff.	Means. 2nd Diff.
2	483.04	484.24	- 1.20	$F(3) - F(2)$	483.64
3	722.70	721.42	+ 1.28	$F(4) - F(3)$	722.06
4		956.98		$F(5) - F(4)$	956.98

Table XVI.—Final Term Data of 180 PQR.

m .	$R(m) - Q(m+1)$.	$Q(m) - P(m+1)$.	Diff.	Term Diff.	Means. 2nd Diff.
2	501.89	503.09	- 1.20	$f(3) - f(2)$	502.49
3	748.51	747.23	+ 1.28	$f(4) - f(3)$	747.87
4		990.77		$f(5) - f(4)$	990.77

As in the case of 177 PQR, the second difference of the terms falls a little as m increases. Owing to the absence of $P(2)$ and $R(1)$, the lowest term differences given directly by the data are $F(3) - F(2)$ and $f(3) - f(2)$. Using the approximations $F(m) = B(m - P)^2$ and $f(m) = b(m - \rho)^2$, we have from $F(3) - F(2) = B(5 - 2P) = 483.64$ and $2B = 238.42$, $B = 119.21$ and $P = 112.41 \div 238.42 = 0.471$. This is just under $\frac{1}{2}$, and it is not certain that P would differ from $\frac{1}{2}$ if it were possible to extrapolate to $m = 0$. Similarly, from $f(3) - f(2) = b(5 - 2\rho) = 502.49$ and $2b = 245.38$ we have $b = 122.69$ and $\rho = 110.96 \div 245.38 = 0.453$. This again is just below $\frac{1}{2}$, and the formulæ are not accurate enough to enable us to be certain that ρ differs from $\frac{1}{2}$. Evidently both initial and final terms are of the $\frac{1}{2}$ -quantum type. If we assume $P = \rho = \frac{1}{2}$, we find from $v_0 = Q(1) - F(1) + f(1)$ that $v_0 = 25738.91$.

The intensities of the lines in the Q series and in the two fragments are mutually consistent. The maximum strength in both the Q and the R series is at $m = 3$ and in the P series at $m = 4$. The distribution of intensity resembles that in 157 PQR which has similar moments of inertia. In both bands the values of m for the intensity maxima seem a little high for the moments of inertia.

Perhaps the most remarkable feature of the next band, 181 PQR, is its resemblance to 180 PQR. If Tables XIV and XVII are compared it will be seen that the intensities of corresponding lines in the two bands are in each

case similar to one another. The principal differences are that in 181 P (2) has put in an appearance and R (4) occurs instead of R (2) in 180. The line 26591·22 is also claimed, but rather doubtfully, as 177 P (5).

Table XVII.—Series No. 181 P (*m*).

<i>m</i> .	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
2								3907·54	25584·35 (<i>p</i>)		
3								3949·38	25313·32 (<i>r</i>)	271·03	7·24
4								3993·27	25035·05 (<i>o</i>)	278·27	6·69
5								4039·25	24750·09 (<i>r</i>)	284·96	

Series No. 181 Q (*m*).

1								3869·22	25837·72 (0)		
2								3869·99	25832·58 (0)	5·14	5·73
3		++	O				S	3871·62 E ₂ ?	25821·71 (2)	10·87	5·92
4								3874·14	25804·92 (<i>o</i>)	16·79	4·24
5								3877·30	25783·89 (<i>p</i>)	21·03	

Series No. 181 R (*m*).

<i>m</i> .											
3								3759·57	177 P (5)	26591·22 (<i>q</i>)	
4								3724·89	E ₃	26838·72 (<i>g</i>)	247·50

* E₂ ? denotes that the evidence is not clear as to whether the line enhanced in 2nd type discharge is this or $\lambda = 3872\cdot38$.

The term data are given in Tables XVIII and XIX. The second differences in the term numbers rise slightly as *m* increases. F (5) might be a little abnormal. This would account for the increased jump from F (4) — F (3)

Table XVIII.—Initial Term Data of 181 PQR.

<i>m</i> .	R (<i>m</i>) — Q (<i>m</i>).	Q (<i>m</i> +1)—P (<i>m</i> +1).	Diff.	Term Diff.	Means.	2nd Diff.
1		248·23		F (2) — F (1)	248·23	
2		508·39		F (3) — F (2)	508·39	260·16
3	769·51	769·87	— 0·36	F (4) — F (3)	769·69	261·30
4	1033·80	1033·80	+ 0·00	F (5) — F (4)	1033·80	264·11

Table XIX.—Final Term Data of 181 PQR.

<i>m</i> .	R (<i>m</i>) — Q (<i>m</i> +1).	Q (<i>m</i>) — P (<i>m</i> +1).	Diff.	Term Diff.	Means.	2nd Diff.
1		253·37		$f(2) - f(1)$	253·37	265·89
2		519·26		$f(3) - f(2)$	519·26	
3	786·30	786·66	- 0·36	$f(4) - f(3)$	786·48	267·22
4	1054·83	1054·83	+ 0·00	$f(5) - f(4)$	1054·83	268·35

to F (5) — F (4) as compared with the others, and also for the drop in the third second difference of 181 Q (*m*) (Table XVII). However, there are not enough lines to be certain about this. From B (3 — 2 P) = F (2) — F (1) = 248·23 and 2 B = 260·16, we find B = 130·08 and P = 0·546 and from *b* (3 — 2 ρ) = *f* (2) — *f* (1) = 253·37 and 2 *b* = 265·89 we have *b* = 132·95 and = 0·548. As the functions F (*m*) and *f* (*m*) are both very similar for this band, it is clear that P and ρ have practically identical values even if they differ from $\frac{1}{2}$. If we put P = ρ = 0·547 we obtain from $\nu_0 = Q(1) - F(1) + f(1)$ the value 25838·31. Both initial and final terms are evidently of the half-quantum type. The moments of inertia are not identical with those for any other known bands, and the values of B and *b* seem high for intensity maxima at *m* = 3 or 4, as is the case in each of the three series.

The following fragment seems to be connected with the two preceding :—

Table XX.—Series No. 182 P (*m*).

<i>m</i> .	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
3								3937·42	25390·18 (<i>r</i>)	288·08	7·35
4								3982·61	25102·10 (1)		
5								4031·17	24806·67 (<i>q</i>)	295·43	

Series No. 182 Q (*m*).

1								3856·51	25930·18 (<i>r</i>)	7·73	6·84
2								3857·66	25922·45 (<i>qd</i>)		
3								3858·74	25907·88 (1)	14·57	

Series No. 182 R (*m*).

2?								3780·6	26443—(<i>s</i>)		
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(*s*) denotes intensity less than (*r*).

None of the lines in this fragment have been recorded as weakened or enhanced in the electron discharges. Except that corresponding lines are weaker, the distribution of intensity is similar to that in 180 PQR and 181 PQR, the only lines of any strength being P (4) and Q (3). The assignation of 26443 — to 182 R (2) is doubtful, and rests only on an approximate agreement with the combination principle. This is an extremely weak line which is too faint to measure properly. As the faint lines P (2) Q (4) and Q (5) which are present in 180 or 181 have disappeared in 182, it is quite likely that the weak fragments of the R branch present in 180 and 181 have entirely disappeared.

Since there are so few lines in this fragment, it may be permissible to extrapolate the wave-numbers of 182 P (2), 182 Q (4) and 182 Q (5) from the values in Table XX, assuming the second differences 7·35 and 6·84 to remain constant. As the extrapolated intervals are small, the values so obtained must be fairly close to the true wave-numbers of the missing lines. They are found to be P (2) = [25670·91], Q (4) = [25886·47] and Q (5) = [25858·22]. With these numbers and those in Table XX the term data shown in Tables XXI and XXII can be deduced. All extrapolated wave-numbers and all quantities which involve the use of any extrapolated wave-number in their deduction are distinguished by being enclosed in square brackets.

Table XXI.—Initial Term Data of 182 PQR.

m .	$R(m) - Q(m)$.	$Q(m+1) - P(m+1)$.	Diff.	Term. Diff.	Means.	2nd Diff.
1		[251·54]		F (2) — F (1)	[251·54]	
2	520·55	517·70	+2·85	F (3) — F (2)	517·70	[266·16]
3		[784·37]		F (4) — F (3)	[784·37]	[266·67]
4		[1051·55]		F (5) — F (4)	[1051·55]	[267·18]

Table XXII.—Final Term Data of 182 PQR.

m .	$R(m) - Q(m+1)$.	$Q(m) - P(m+1)$.	Diff.	Term. Diff.	Means.	2nd Diff.
1		[259·27]		$f(2) - f(1)$	[259·27]	
2	535·12	532·27	+2·85	$f(3) - f(2)$	532·27	[273·00]
3		805·78		$f(4) - f(3)$	805·78	273·51
4		[1079·80]		$f(5) - f(4)$	[1079·80]	[274·02]

The values of $F(3) - F(2)$ and of $f(3) - f(2)$, which involve the unsatisfactory line $R(2) = 26443\cdot—$, have not been used in the last two columns of these tables. There are not enough data to determine the initial values B and P without using the extrapolated values, but on the whole the appearance of the data got by the extrapolation seems satisfactory and, in any event, we cannot be far wrong in putting $2B = [266\cdot6]$. This, together with $B(5 - 2P) = 517\cdot70$, gives $B = [133\cdot3]$ and $P = [0\cdot558]$. With the final terms we do not need to use the extrapolated values. Taking $2b = 273\cdot51$, we have $b = 136\cdot76$ and $\rho = 0\cdot554$. As in the case of 181 PQR, P and ρ are equal and not far from $\frac{1}{2}$, so that both initial and final terms are of half-quantum type. Putting $P = \rho = 0\cdot556$, we get from $\nu_0 = Q(1) - F(1) + f(1)$ the value $\nu_0 = 25930\cdot86$. The value of the initial B for 182 PQR is practically the same as that of the final b for 181 PQR, and the difference of $B - b$ is almost the same for both bands (and also for 180 P, Q R). A parallel instance of bands having similar relations is furnished by 161 P, 169 Q, 164 R and 163 P, 169 Q, 162 R.* The final moment of inertia is very close to that of 158 $R^1(m)$ *ante*. As in the preceding bands, the maximum intensity of the lines for the branches of this fragment is at high values of m for the apparent moments of inertia of the molecules concerned.

The next band, 183 PQR, contains one line recorded as enhanced in the first-type discharge, viz., 27004·03 assigned to $R(3)$. $Q(1) = 25627\cdot88$ is

Table XXIII.—Series No. 183 P (m).

m .	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
1								3955·25	25275·76 (0)		
2								4013·15	24911·07 (0)	364·69	7·77
3								4074·07	24538·61 (1)	372·46	7·71
4								4138·18	24158·44 (r)	380·17	

Series No. 183 Q (m).

1								3900·90	26 R (4) 25627·88 (r)		
2								3902·67	25616·26 (0)	11·62	8·38
3								3905·72	25596·26 (r)	20·00	8·99
4								3911·25	25567·27 (p)	28·99	

* O. W. Richardson, 'Roy. Soc. Proc.,' A, vol. 108, p. 553 (1925).

Table XXIII—(contd.).
Series No. 183 R (*m*).

<i>m</i> .	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
1	(1)	(2)	(3)	(4)	(5)	(6)	(7)	3796·63	177 P (6) 26331·73 (2)		
2			Missing								
3								3702·10	E ₁ 27004·03 (1)	319·94	
4								3658·75	27323·97 (<i>r</i>)		

also claimed by a doubtful series, which has been called 26 R (*m*), and 26331·73 is claimed as 177 P (6), where, however, it is much too strong. It appears that this band is one in which the intensities of successive lines are alternately strong and weak. The odd numbers are the weaker in the Q series and the even numbers in the P and R series. The line 183 R (2) is missing altogether.

The term data are given in Tables XXIV and XXV. With the numeration given in the first columns, and using the same approximate formulæ for the term numbers as in dealing with the preceding bands, we get from B (3 — 2 P) = F (2) — F (1) = 704·52 and 2 B = 353·13 the values B = 176·57 and P = — 0·495.

Table XXIV.—Initial Term Data for 183 PQR.

<i>m</i> .	R (<i>m</i>) — Q (<i>m</i>).	Q (<i>m</i> + 1) — P (<i>m</i> + 1).	Diff.	Term Diff.	Means.	2nd Diff.
1	703·85	705·19	—1·34	F (2) — F (1)	704·52	353·13
2		1057·65		F (3) — F (2)	1057·65	
3	1407·77	1408·83	—1·06	F (4) — F (3)	1408·30	348·40
4	1756·70			F (5) — F (4)	1756·70	

Table XXV.—Final Term Data for 183 PQR.

<i>m</i> .	R (<i>m</i>) — Q (<i>m</i> + 1).	Q (<i>m</i>) — P (<i>m</i> + 1).	Diff.	Term Diff.	Means.	2nd Diff.
1	715·47	716·81	—1·34	<i>f</i> (2) — <i>f</i> (1)	716·14	361·51
2		1077·65		<i>f</i> (3) — <i>f</i> (2)	1077·65	
3	1436·76	1437·82	—1·06	<i>f</i> (4) — <i>f</i> (3)	1437·29	359·64

Similarly, from *b* (3 — 2 ρ) = *f* (2) — *f* (1) = 716·14 and 2 *b* = 361·51, we find *b* = 180·76 and ρ = — 0·482. Substituting these values in *v*₀ = Q (1) —

$F(1) + f(1)$, we obtain $\nu_0 = 25630.27$. Both initial and final states are evidently of half-quantum type, with P and ρ each close to $-\frac{1}{2}$ with the numeration given in Tables XXIII–XXV. If all the values of m were increased by unity, the negative sign of P and ρ would, of course, disappear.

The alternation in intensity of the lines of this band is interesting. If the alternate stronger lines $P(1), P(3), Q(2), Q(4), R(1), R(3)$ are tabulated they are found to involve the final states $f(1), f(2), f(3), f(4)$ indiscriminately, but they only include the initial states $F(0), F(2)$ and $F(4)$. Similarly, the alternate weak lines include all the final states $f(1), f(2), f(3), f(4)$, but only the initial states $F(1), F(3)$ and $F(5)$. It appears from this that the alternation in intensity is due to something which favours the even numbers (as enumerated) in the initial states, but that there is no indication of any similar restriction on the final states. The presence of $P(1)$ and absence of $Q(0)$ and $R(0)$ suggest the prohibition of the final, $f(0)$ but not of the initial $F(0)$.

The value of $B\ 176.57$ may be compared with Ca for $11\ R'(m) = 177.76$, B for $171\ P\ 170\ Q\ 162\ R = 174.06$, B for $163\ P\ 170\ Q\ 164\ R = 174.29$, Ca for $152\ R(m) = 175.30$, b for $84\ PQR = 173.70$, and Ce for $186\ R(m) = 175.15$ and the value of $b\ 180.76$ with Ce for $10\ P'(m) = 183.24$, b for $161\ P\ 169\ Q\ 164\ R = 181.50$, B for $163\ P\ 169\ Q\ 162\ R = 181.40$, Ca for $152\ R'(m) = 182.39$, B for $84\ PQR = 183.43$ and Ca for $186\ R(m) = 180.63$. Some of these are so near the values for $183\ PQR$ that a more refined theory of the phenomena than that which has been used would be required to distinguish them. The intensity distribution among the lines seems not unreasonable when allowance is made for the alternation in intensity already discussed.

The following lines may perhaps be briefly mentioned, though the arrangement outlined is far less certain than that of any of the series previously considered in this paper. In fact, the suggested grouping is merely a guess, founded on the fact that there are very few lines in this part of the spectrum, and the number of alternative arrangements is rather limited.

Table XXVI.—No. 179 $P_1(m)$.

m .	Properties.							W.L. in Air.	Wave Number (Int.).	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
2								3329.50	30025.97 (r)	$\left. \begin{array}{l} 255.12 \\ 323.49 \end{array} \right\} 68.37$	
3								3358.03	29770.85 (r)		
4		+						3394.92	29447.36 (1)		

Table XXVI—(contd.).

No. 179 Q₁ (m).

<i>m.</i>	Properties.							W.L. in Air.	Wave Number (Int.)	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
1								3295.48	30335.85 (r)	> 66.67	
2								3302.74	30269.18 (r)		

No. 179 P₂ (m).

2								3331.41	30008.76 (r)	> 254.21 > 318.38	> 64.17
3								3359.87	29754.55 (rd)		
4		+						3396.21	29436.17 (0)		

No. 179 Q₂ (m).

1								3298.2	30311.3	> 68.21	
2								3305.59	30243.09 (r)		

Table XXVII.—No. 188 P (m).

<i>m.</i>	Properties.							W.L. in Air.	Wave Number (Int.)	1st Diff.	2nd Diff.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)				
2								3499.78	28565.06 (r)	> 443.25	
3		+						3554.95	28121.81 (0)		

No. 188 Q (m).

1		+						3404.49	29364.61 (0)	> 124.44 > 189.56	> 65.12
2		+						3390.12	29489.05 (0)		
3		+						3368.47	29678.61 (0)		

No. 188 R (m).

0								3370.87	29657.48 (rd)	> 632.98	
1								3300.42	30290.46 (r)		

If these allocations are correct, we get for 179 P₁Q₁B = 60.04, $b = 94.23$, $P = -0.525$, $\rho = -0.144$ and $\nu_0 = 30330.0$, and for 179 P₂Q₂B = 60.92, $b = 93.00$, $P = -0.424$, $\rho = -0.1268$ and $\nu_0 = 30305.4$. With these values of B and b may be compared $b = 57.59$ for 1P 28Q 101R, $Ca = 61.89$ for 52 P (m) and $Ca = 90.94$ for 153 P (m). For 188 PQR the data for the

final terms suggest a moment of inertia varying rapidly with m , and only very rough values of the quantities can be deduced. It appears, however, that both P and ρ are close to zero, B and b are very high and probably about 280 and 250 respectively, and ν_0 is about 29,330. These values of B and b are larger than those for Fulcher's second band, and similar to the highest values yet found for any other known bands. The fragment 188 PQR gives the one possible combination, viz., $R(1) - Q(1) = 925\cdot85$ and $Q(2) - P(2) = 923\cdot99$. The error 1.86 is probably not excessive for these lines.

These arrangements leave only eight known lines, all very weak, in the region from $\nu = 27700$ to $\nu = 30400$, where the lines measured up to the present come to an end. Of these the six lines $\lambda 3514\cdot14$, $3510\cdot44$, $3502\cdot54$, $3499\cdot78$, $3487\cdot6$ —, $3483\cdot97$ are huddled up together between the narrow limits of $\nu 28448\cdot37$ and $\nu 28694\cdot73$. They are in three pairs with the doublet distances $\nu 29\cdot93$, $\nu 27\cdot64$ and $\nu 29\cdot97$. They are almost certainly a self-contained fragment of something, but it is difficult to say of what. They might be two P or R branches with a high moment of inertia. The two remaining lines are $\lambda 3345\cdot08 = \nu 29886\cdot07$ (r) and $\lambda 3315\cdot32 = \nu 30154\cdot36$ (q) and may be a continuation of something in the unexplored part beyond the present ultra-violet limit. It is intended to examine this region in more detail shortly.

A summary of the principal values from the sequences discussed in this paper is given in Table XXVIII. The strong tendency of the values of P and ρ to approximate to the values $0 \pm \frac{1}{2}$ and 1 is, perhaps, the most notable feature. The proportion of bands with half-quantum term numbers is quite high. If, excluding 179 and 188 at the end of Table XXVIII, we take the 20 combinations for which P and ρ have now been approximately determined in this and preceding papers, we find that the proportion of values of P between $+0\cdot4$ and $+0\cdot6$ and between $-0\cdot4$ and $-0\cdot6$ is 13 : 20, and of ρ between the same limits it is 9 : 20. If the values of P and ρ were spread evenly over the range -1 to $+1$, these proportions would be 4 : 20. So far as I can see, there is nothing in the methods of selecting the lines which can favour values of P and ρ in the neighbourhood of $\pm 0\cdot5$ rather than elsewhere, in the range from -1 to $+1$, so that it seems that a preponderance of half-quantum term numbers must be a feature of this spectrum.

In spite of the progress made, our knowledge is still too fragmentary for anything very definite to be said about the connection between the ν_0 s. The successive values of ν_0 for 183, 180, 181 and 182 look like four lines of a sequence approaching a limit, but there is nothing as yet to indicate which of the other values of ν_0 are connected with them.

Table XXVIII.

Series No.	ν_0 .	B.	b .	P.	ρ .	Ca.	Ce.	Ca—Ce.
157 PQR	16733 —	≈ 111.5	≈ 115	$\left\{ \begin{array}{l} -0.478 \\ \approx -\frac{1}{2} \end{array} \right\}$	≈ -0.306			
153 P (m)	17075.90					90.94	114.04	— 23.10
or	or					or	or	or
153 P' (m)	17172.10					79.39	102.49	— 23.10
156 Q (m)	17495			≈ 1	≈ 1			18.5
158 R (m)	16051.63					140.79	138.64	2.15
or	or					or	or	or
158 R' (m)	15912.45					139.72	137.57	2.15
154 Q (m)	16802			≈ 1				58.15
186 R (m)	16621.75					180.63	175.15	5.48
or	or					or	or	or
186 R' (m)	16445.23					177.89	172.41	5.48
177 PQR	27614.55	152.7	148.5	0.83	0.845			
180 PQR	25738.91	119.21	122.69	$\left\{ \begin{array}{l} 0.471 \\ \approx \frac{1}{2} \end{array} \right\}$	$\left\{ \begin{array}{l} 0.452 \\ \approx \frac{1}{2} \end{array} \right\}$			
181 PQR	25838.31	130.08	132.95	0.546	0.548			
182 PQR	25930.86	[133.3]	136.75	[0.558]	0.554			
183 PQR	25630.27	176.57	180.76	— 0.495	— 0.482			
179 P ₁ Q ₁ †	30330.0	[60.04]	94.23	[— 0.525]	— 0.144			
179 P ₂ Q ₂ †	30305.4	[60.92]	93.00	[— 0.424]	— 0.127			
188 PQR†	≈ 29330	≈ 280	≈ 250	≈ 0	≈ 0			

† These are more doubtful than the others.

[] Square brackets denote that one or more extrapolated lines have been used in deriving the data.

In these four bands the Q series are more definite than the other branches, and the R branches in particular are relatively much more doubtful. If the frequencies of the lines of the Q branches are set out so that corresponding lines come adjacent to each other, the successive differences between the frequencies of adjacent lines show regular progressive differences with changes of m . This is shown in Table XXIX, where the numeration for 180 182 Q (m) is the same as that in the preceding tables in this paper, but the numeration of 183 Q (m) is for each line 1 higher than in Table XXIII. This brings the strongest line of each series into the same horizontal row and brings about a general correspondence as regards the intensities of the lines. It also makes P and ρ for 183 PQR approximately equal to $+\frac{1}{2}$, as is the case for the other three bands,

instead of $-\frac{1}{2}$ approx. When this is done the frequency differences of corresponding lines are as shown in columns 3, 5 and 7 of Table XXIX. The successive vertical differences of these horizontal differences are for the third column 7.23, 5.81, 4.80; for the fifth column, 8.43, 7.98, 9.02, 12.76; for the seventh column, 2.59, 3.70. These differences all show a regular progression within the limits of error of the measurements. This regularity is only put forward here as evidence in favour of the reality of the series under consideration, and not as requiring the change in the numeration of 183 PQR from that of Table XXIII to that of Table XXIX. For the present it seems better to retain the enumeration of Table XXIII, as the distribution of intensity among the lines then shows a better relative agreement with the low moment of inertia which the term differences give for this band.

Since the preceding part of this paper was written the following papers dealing with the secondary hydrogen spectrum have come to my attention, viz.: MacLennan and Shrum, 'Trans. Roy. Soc. Canada,' vol. 18, p. 177 (1924); Goos, 'Zeits. für Physik,' vol. 31, p. 229 (1925); and Dieke, 'Zeits. für Physik,' vol. 32, p. 180 (1925). MacLennan and Shrum have examined this spectrum in a Geissler tube with a thin-walled capillary immersed in liquid hydrogen,

Table XXIX.—Frequencies of lines 180–183 Q (*m*).

<i>m</i>	Series 183 Q (<i>m</i>).	180 Q (<i>m</i>).	181 Q (<i>m</i>).	182 Q (<i>m</i>).
1.....		25738.04 (0)	25837.72 (0)	25930.18 (r)
			99.68	92.46
2.....	25627.88 (r)	25724.47 (0)	25832.58 (0)	25922.45 (<i>gd</i>)
		96.59	108.11	89.87
3.....	25616.26 (0)	25705.62 (3)	25821.71 (2)	25907.88 (1)
		89.36	116.09	86.17
4.....	25596.26 (r)	25679.81 (<i>g</i>)	25804.92 (0)	
		83.55	125.11	
5.....	25567.27 (<i>p</i>)	25646.02 (<i>p</i>)	25783.89 (<i>p</i>)	
		78.75	137.87	

and have published lists of lines which they have observed to be enhanced, weakened, or missing under these conditions. Goos has examined the variation with temperature and pressure of the intensities of some of the chief Fulcher lines and a few other lines in their neighbourhood, in a Geissler-tube discharge, the range of temperature being from 87° to 495° K. A large proportion of the lines recorded by MacLennan and Shrum as affected by temperature are Fulcher

lines. Of these all the enhanced lines belong to the groups S_7 to S_3 or ξ_3 ,* and the weakened lines to S_2 to S_{-1} or ξ_2 to ξ_{-1} , the relative weakening increasing as S_{-1} or ξ_{-1} is approached. The quantitative measurements of Goos also establish weakening of the lines of S_2 and S_1 compared with S_3 as the temperature is reduced.

These facts, in conjunction with the critical discussion of the numerical data given by Curtis,* would seem to establish the reality of Allen's† vertical series in these bands. Dieke, however, goes further than this. He asserts that, inasmuch as the individual lines of S_3 , the strongest horizontal series, undergo no perceptible relative change in intensity among themselves over the range 19° K. to 495° K., whereas there is a marked relative strengthening with rise of temperature in going from S_3 to S_1 when corresponding lines of each horizontal series are compared, it follows that the horizontal series such as S_3 , S_2 or S_1 must be oscillational series and the vertical series of Allen rotational series of the Q type. This would involve an inversion of the arrangement proposed by Curtis,‡ who made the horizontal series rotational series of the P type and the vertical series oscillational series.

It appears to me, however, that the argument from the temperature variation of the intensities of the lines of a series may not be capable of distinguishing between their translational or rotational origin. In any series the intensity of a line is proportional to three factors, viz., the probability of transference from the given initial to the given final state, the energy $h\nu$ in a quantum of the line, and the number of systems in the given initial state. The first two factors do not involve the temperature, and the last involves it only through the factor $e^{-w/kT}$, where w is the energy in the initial state. This formula is the same whether the energy w is supposed to be due to oscillations or to rotations. Whether we suppose the horizontal series to be rotational and the vertical series oscillational (like Curtis), or the horizontal series to be oscillational and the vertical series rotational (like Dieke), the widely spaced horizontal series, which has a correspondingly higher degree of energy per quantum, should be less susceptible at low temperatures to changes of temperature than the closely grouped vertical series. If these bands consist only of a set of branches of the same kind, either P or Q, with no other associated branch or set of branches, it would seem to be very difficult to decide whether the horizontal series are

* Curtis, 'Roy. Soc. Proc.,' A, vol. 107, p. 584 (1925).

† Allen, 'Roy. Soc. Proc.,' A, vol. 106, p. 69 (1924).

‡ *Loc. cit.*

rotational and the vertical oscillational or *vice versa*. In an earlier paper Dieke* has proposed to arrange Fulcher's S_7 and S_4 lines with a few other lines as R series in conjunction with Allen's vertical series as Q series. If this association is real it would seem to establish the rest of his position.

Of the remaining lines in MacLennan and Shrum's tables a large proportion, perhaps the majority, are to be found in the series published in this and preceding papers. The number of both enhanced and weakened lines is surprisingly small, and it seems as though the distribution of rotational impulse among the emitters of this spectrum has more to do with the conditions of electrical excitation than with the temperature of the gas, at temperatures between 19° K. and 300° K. The incidence of the lines on published series is not very regular, although there appear to be indications of a general tendency for the weakened lines to favour higher quantum numbers, and *vice versa*, but the selection of the lines seems very irregular. Curiously there seems a tendency for Q (1) lines to appear in the lists of weakened and missing lines. Thus Q (1) of Kiuti's series is given as much weakened and Q (2) as weakened, in the weakened table. Q (2) is also included as missing in the table of missing lines. Other lines missing at 19° K. which have been assigned to Q (1) are $6329\cdot60 = 159$ Q' (1), $5956\cdot42$ (3) = 157 Q (1), $5716\cdot00$ (3) = 156 Q (1), $5616\cdot24$ (0) = 169 Q (1), $4751\cdot59$ (1) = 110 Q (1), but $5949\cdot90$ (9) = 154 Q (1) = 186 R (2) is enhanced. However, 186 R (m) seems to be a series which is enhanced like Fulcher's S_3 and Σ_3 at 19° K, and this line might not belong to 154 Q (m).

There seems to be some correspondence between MacLennan and Shrum's conditions and the conditions of the first-type discharge. In my list of lines enhanced in this discharge there are 17 lines in the region which overlaps with MacLennan and Shrum's list; of these 17, nine occur in their list, and my list includes none of their weakened or missing lines. The Fulcher lines in my list of enhanced lines are $15552\cdot41$ (5) (S_3), $15622\cdot02$ (6) (S_6), $15787\cdot28$ (5) (S_2), $15859\cdot93$ (3) (S_4), $15870\cdot09$ (7) (S_6), $16121\cdot59$ (5) (S_4), $16330\cdot66$ (10) (S_3), $16393\cdot66$ (6) (S_4), $16596\cdot41$ (7) (S_2), $16611\cdot43$ (10) (S_3), $18445\cdot52\cdot52$ (6) (Σ_3) and $18851\cdot49$ (8) (Σ_3).

Turning to the lines weakened in the first-type discharge, there are 82 in my list in the overlapping region; of these, 23 are given by MacLennan and Shrum as weakened or missing and 3 as enhanced. The Fulcher lines which are given as weakened in the first-type discharge in my table are $16294\cdot53$ (8)

* 'Amsterdam Acad. Proc.,' vol. 27, p. 490 (1924).

(S_1), 16692.04 (5) (S_6) and 18394.72 (5) (Σ_1). The strengthening of the low-quantum members and the weakening of the high-quantum members of Allen's vertical series in the first-type discharge is thus very noticeable. The difference as regards Fulcher bands is that in the first-type discharge the series S_2 is added to the lines enhanced at 19° K., whereas it is unaffected according to the observations of MacLennan and Shrum. This difference is of the kind to be expected from the difference in temperature. It is not certain that the line 16692.04 (5) (S_6) really belongs to Fulcher's bands.

It again gives me great pleasure to thank Mr. W. E. Williams for the assistance he has given me in the critical examination of a number of the lines.

Summary.

In this paper a classification of 132 additional lines of the secondary hydrogen spectrum is proposed. About half the constants which correspond to the moments of inertia of the molecules emitting the proposed series coincide with values which have already appeared in bands previously proposed, to within the accuracy to which they can be determined. Up to the present, 20 combinations have been found leading to 40 sets of term numbers, of which 22, or more than half, are of half-quantum type. It is pointed out that there is a close correspondence between the behaviour of the lines of Fulcher's bands in the first-type discharge and their behaviour in a Geissler-tube discharge immersed in liquid hydrogen, as recorded by MacLennan and Shrum.

On the Excitation of the Band Spectrum of Helium.

By T. R. MERTON, F.R.S., and J. G. PILLEY, B.A.

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It is now generally agreed that the band spectrum of helium, which was first observed by Curtis ('Roy. Soc. Proc.,' A, vol. 89, p. 146, 1913) and by Goldstein ('Verh. d. Deutsch. Phys. Gesell.,' vol. 15, p. 402, 1913), is to be attributed to some molecule of helium. This band spectrum is peculiar in the fact that the heads of the bands have been shown by Fowler ('Roy. Soc. Proc.,' A, vol. 91, p. 208, 1915) to follow the law usually associated with line spectra, though the individual lines composing the bands can be represented by the parabolic arrangement appropriate to band series. More recently, Curtis has carried out a series of investigations ('Roy. Soc. Proc.') on the structure of the bands in terms of the quantum theory. Attention may here be drawn to two peculiarities in the spectrum. There is one isolated band with a head at about $\lambda = 5733$ A., which is degraded to the violet, whilst all the remaining bands are degraded to the red. Also Goldstein (*loc. cit.*) observed a number of faint band lines in the region about $\lambda = 5390$ A. to $\lambda = 5270$ A., which were not recorded in Curtis's paper (*loc. cit.*).

It is well known that in vacuum tubes excited by uncondensed discharges only faint traces of the principal band heads are visible in the positive column though the complete band spectrum appears in the negative glow. The band spectrum can be excited with much greater intrinsic brightness by using a discharge tube with a wide tube in place of the usual capillary, and exciting it by means of a discharge from an induction coil or transformer, with a condenser in parallel and a small spark gap in series with the discharge tube, the band spectrum under these conditions appearing throughout the tube. There appears to be an optimum length of spark gap and the spectrum tends to become weaker when the length is increased beyond a certain point. Curtis (*loc. cit.*) has found that the band spectrum is not strongly developed at low pressures, and this condition appears to be independent of other conditions of excitation. In the present investigation we have found that under certain conditions the band spectrum can be greatly modified. It was observed that when a vacuum tube, containing pure helium, which had been made with the capillary in several sections of different bore, was excited with an uncondensed discharge the narrowest section, which was of the finest thermometer tubing that could be worked conveniently in the blowpipe, showed nothing but the

line spectrum, but in the wider sections on either side the band spectrum was quite strongly developed. This seems to show that a high-current density is not an essential condition for the excitation of the band spectrum, but it was remarkable that with these tubes it appeared in the wider parts, where it would not have been seen if the capillaries had not been provided with a section of narrow bore.

We have examined the effect on the band spectrum of varying the excitation, and have found that some bands which are usually very inconspicuous become so much stronger under certain conditions that it seems almost as if, in what is regarded as the helium band spectrum, two separate systems are superposed, the relative intensities of which can to a great extent be controlled by the discharge conditions. In particular, the group of green band lines which were seen faintly by Goldstein (*loc. cit.*), but not recorded by Curtis (*loc. cit.*), is the most conspicuous of the bands which could be selectively enhanced. For convenience, this band system will be referred to as the "green band," in distinction to the bands arranged in series by Fowler (*loc. cit.*). The intrinsic brightness of this spectrum has not been great enough to enable us at present to determine the wave-lengths from high-dispersion photographs, but a provisional list of the wave-lengths of the lines of this band, for identification, is given in the following table:—

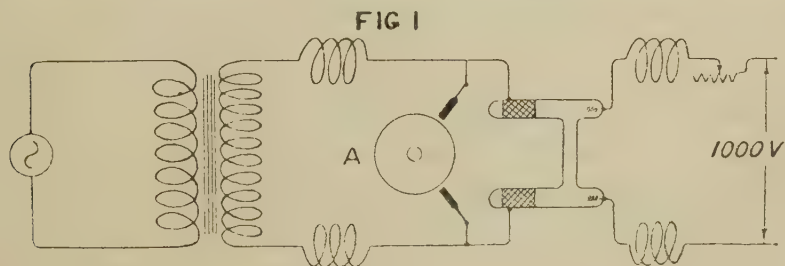
λ	Int.	λ	Int.
5386.5	1	5316.4	2
5381.9	3	5311.9	7
5377.8	4	5305.4	4
5372.0	6	5299.2	3
5365.7	5	5298.3	2
5358.7	4	5293.0	6
5346.8	1	5287.8	4
5338.2	4	5282.3	5
5329.1	5	5277.8	0
5319.5	4	5276.6	6

The selective enhancement of certain band groups was first observed in a comparison of the spectrum of the cathode glow, with continuous excitation, and that of the positive column with a condenser and a small spark gap, the "green band" being fairly conspicuous under the former conditions. Attempts to modify the spectrum by varying the capacity of the condenser and the length of the spark gap were to some extent effective, but it was found in a series of experiments in which the tubes were excited by high-frequency

discharges that under certain specified conditions the "green band" could be made to appear with unusual brilliance. The description of the results may be confined to observations made with one particular discharge tube, which was of the H type and contained helium at a pressure of 30 mm.; it was provided with aluminium electrodes of the usual type, and the capillary was of about 3 mm. internal bore. Several different methods of generating high-frequency discharges were used, and the frequency was varied between wide limits. One method involved the use of a thermionic valve, and although the highest frequencies obtained by means of spark discharges could not be attained by this method, it offered the advantage of giving undamped waves. A $\frac{1}{4}$ -kilowatt valve was used, and with the arrangement adopted the frequency was varied from about 10^4 per second to a maximum which was estimated as between 10^7 and 10^8 . Within this range of frequency the spectrum was not appreciably different from that produced by excitation with a continuous discharge, the principal band heads being only just visible, and the same results were obtained whether the inside or outside electrodes were used.

In another series of experiments high-frequency oscillations were generated with the aid of a simple form of Poulsen arc. With a primary inductance which gave a frequency of 10^6 (measured with a wave-meter) the spectrum of the discharge was similar to that obtained by the valve method, but when the primary was reduced to a few turns of thick copper tube the behaviour of the arc became somewhat irregular and the complete band spectrum appeared, with the "green band" fairly conspicuous. With this arrangement it is probable that the discharge did not consist of truly continuous waves, but rather of a series of oscillatory discharges in close succession.

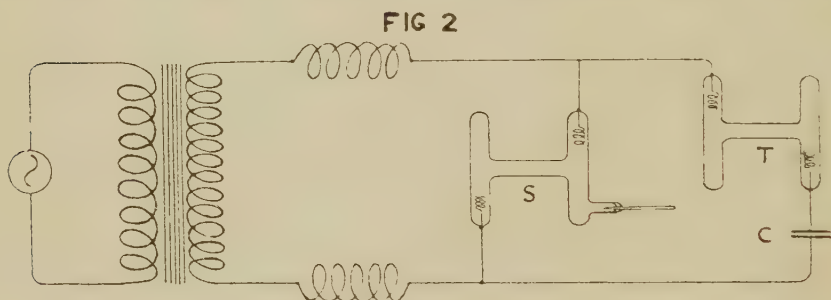
Experiments were made with several arrangements involving spark discharges, and a further relative enhancement of the "green band" was observed when the tube was excited by means of a small Tesla transformer. A more effective arrangement is shown in fig. 1. Here the inductance of the high-frequency



circuit was reduced to a minimum, and the capacity was only that of the leads and the small pieces of copper foil which served as outside electrodes to the discharge tube. A high-speed rotating spark gap A effectively prevented arcing, and with this arrangement the "green band" was distinctly stronger than the green doublet band on the more refrangible side of it.

A method was found by which the variation of the spectrum could be easily controlled. It was found that a spark gap in air was irregular and unsatisfactory for very short spark lengths, and the spark gap was therefore replaced by a discharge tube containing hydrogen, which was provided with a palladium tube regulator so that the pressure of hydrogen in the tube could be varied by heating the regulator in the base of a Bunsen flame where the partial pressure of hydrogen is high, or alternatively in the tip of the flame where it is extremely low. This arrangement provided a very convenient adjustable short spark gap, which was very regular in its action.

The arrangement adopted is shown in fig. 2, in which S is the hydrogen



tube used in place of the spark gap, T the helium tube, and C a variable condenser. This arrangement probably yields a rapid series of damped oscillations and the maximum potential applied to the tube T is evidently dependent on the sparking potential of the tube S. The following phenomena were observed. Starting with a rather high pressure in S there was no discharge visible in T, but as the hydrogen was gradually removed from S and its sparking potential thus increased, a point was reached at which T showed only the arc spectrum of helium, with the very faint traces of the band heads which are always seen in pure helium. With a slightly lower pressure in S the band spectrum appeared suddenly, with the "green band" very conspicuous and considerably more intense than the more refrangible doublet band. At lower pressures in S the latter became much stronger and the "green band" faded out and ultimately became barely visible.

The phenomena can perhaps be explained on the following lines : The energy required to excite the band spectrum must be somewhat greater than that required to excite the arc spectrum, the "green" band spectrum requiring a smaller energy than the remainder of the band spectrum. For this reason the spectrum cannot be fully developed in the positive column when the tube is excited by a continuous or low-frequency alternating discharge, since the potential gradient in the positive column (the resistance of which is very small) is not sufficiently high. In the neighbourhood of the cathode, where the potential gradient is much steeper, electrons are able to acquire sufficient energy to excite the band spectrum.

Our experiments seem to show that the band spectrum can be excited in the positive column by discontinuous, but not by continuous, high-frequency oscillations. With continuous oscillations the interval of time between the breaking and the restriking of the arc is so short that the resistance of the tube never rises in that interval to a value much in excess of what its resistance would be if the tube were excited by a continuous discharge. With a succession of damped discharges it may be supposed that the resistance of the tube rises between successive discharges to a much higher value, and when a fresh discharge is started the charge on the electrodes increases so rapidly that the rate of increase of the number of ions in the tube is not sufficiently rapid to prevent a considerable rise in the potential gradient, with the result that during this very short interval of time the electrons are able to acquire much greater velocities.

The following experiment seems to be in accordance with this view. The tube was excited as shown in fig. 1, the complete band spectrum being strongly developed under these conditions, and the internal electrodes shown in fig. 2 were connected through inductances to a small 1,000-volt direct-current generator, which was driven by an electric motor, the speed of which could be controlled by means of a rheostat. It was found that as the intensity of the direct-current, which was superposed on the high-frequency oscillations, was increased the band spectrum gradually disappeared. This result is to be expected, since the resistance of the tube will be maintained at a low value by the passage of the direct current.

These considerations seem to apply in general to the production of spectra by condensed discharges, in which the excitation of spark lines, according to modern views of the origin of spectra, must be ascribed (unless the effects of cumulative ionisation are invoked) to impacts of electrons having certain critical velocities which cannot usually be attained by continuous discharges in the

positive column of a vacuum tube. The high current densities which obtain when powerful condensed discharges are employed, and which give rise to a high concentration of charged particles, would seem to be of importance chiefly in permitting the violation of the principle of selection, owing to the intense local electric fields, the existence of which is demonstrated by the broadening of the lines in accordance with the Stark effect. It has long been known that when an inductance coil is introduced into the circuit of a condensed discharge the effect is to cause a disappearance of the spark lines and to reduce the spectrum to the arc type. The inductance must reduce the rate at which the charge on the electrodes can increase, and, hence, also the maximum potential attained. Further investigation will be required to elucidate fully all the changes in the band spectrum which occur under the different conditions.

We wish to express our thanks to the Department of Scientific and Industrial Research for a grant made to one of us (J. G. P.) during the course of this investigation.

The Scattering of Light by Liquid Boundaries and its Relation to Surface Tension.—Part III.

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(Received, June 3rd, 1925.)

[PLATE 6.]

1. *Relative Scattering-power of Water and other Liquid Surfaces.*

In Part II, the phenomena of the scattering of light by the surface of transparent liquids were described in detail. No reference was, however, made to the case of water, which stands in a special category owing to the exceptional properties of this liquid. Of all known transparent fluids at ordinary temperatures water has the highest surface-tension. Its refractive index is also low, and hence its surface-opalescence may be expected to be very feeble. Fortunately, however, the internal scattering in dust-free water is also very small, being in fact much less than that for any other known liquid, and hence, provided water is obtained dust-free and with an uncontaminated surface, there should be no difficulty in observing its surface-opalescence. This was actually found

to be the case. By using water subjected to repeated slow distillation *in vacuo* in carefully cleaned pyrex glass bulbs, it can be obtained quite pure and dust-free. The surface-opalescence may then be observed, and in agreement with anticipation is found to be very feeble; it exhibits features of polarisation and intensity distribution in different directions very similar to those shown by other liquids.

For inter-comparison of the surface-scattering power of different liquids, the following simple arrangement was adopted. A beam of sunlight from a large heliostat was used and reflected vertically upwards by a second mirror inclined at 45° . The beam passed through two lenses of equal focal length, which were placed as near together as possible and formed images of the sun upon the surfaces of the liquids contained in bulbs, placed one above each of the lenses. By varying the apertures of the lenses, the brightness of the opalescent areas on the two liquid surfaces could be varied till they were estimated to be of equal brightness, as seen by the eye placed below the surfaces at approximately the same angle. The angle of observation chosen was in each case slightly greater than the critical angle, so that the surface-scattering had maximum brightness. By taking the mean of a sufficient number of readings, fairly dependable measures could be obtained of the ratio of surface-brightness, at least in the case of liquids, for which the internal scattering was not so large as to interfere with the judgment of the eye.

A check on the reliability of the measures is obtained by comparing liquid A with liquid B and liquid C, separately, and then comparing liquid B directly against liquid C, and so on. The accuracy of the method could no doubt be greatly improved by using photographic photometry and correcting for the known intensity of the internal scattering, which appears as a superposed effect. Nevertheless, it is felt that visual measures which could be made much more rapidly are not without value and represent the truth with fair accuracy, considering the very difficult nature of the investigation.

The table gives the relative surface-brightnesses of some thirty different liquids in terms of clean water as a standard, together with the surface-tensions and refractive indices (μ_F at 30° C) as given in Landolt's tables. The last column gives the internal (volume) scattering for purposes of comparison from data obtained in the author's laboratory by Mr. K. S. Krishnan.

The measurements show that, generally speaking, the intensity of the surface opalescence increases when the surface-tension is diminished or the refractive index is increased. There are, however, a few anomalous cases, the significance of which remains to be further investigated.

Substance.	Surface Tension.	Refractive index. μ_r	Intensity of surface scattering water = 1.	Intensity of internal scattering water = 1.
Water	72	1.336	1	1

Paraffins and unsaturated hydrocarbons.

Pentane	—	1.353	11.3	5.70
<i>i</i> -pentane	—	1.352	8.9	5.30
Hexane	16.34	1.374	8.5	5.00
Heptane	—	1.387	8.8	5.00
Octane	20	1.396	7.8	4.80
β -iso-amylene	—	1.381	10.8	7.70

Chlorides.

Ethylene chloride	30.10	1.445	3.8	7.20
Chloroform	25.32	1.446	6.3	6.30
Carbon-tetra chloride	24.60	1.462	12.6	5.10
Silicon-tetra chloride	15.80	1.420	7.4	—

Fatty acids.

Formic acid....	35.75	1.372	4.6	6.10
Acetic acid	23.50	1.373	4.9	5.95
Propionic acid	26.6	1.387	5.8	6.20
Butyric	26.7	1.397	6.3	5.95

Oxides.

Ethyl ether	15.27	1.352	7.4	5.00
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Alcohols.

Methyl alcohol	23.00	1.329	4.0	—
Ethyl alcohol	22.00	1.363	5.2	2.90
<i>i</i> -propyl	21.34	1.380	7.2	3.00
Butyl alcohol	24.40	1.400	7.4	3.25
<i>i</i> -butyl alcohol	22.80	1.397	9.3	3.70
Tri-methylcarbinol....	—	1.388	6.6	3.45
Allyl alcohol	23.15	1.419	7.8	6.10
Benzyl alcohol	39.70	1.547	10.0	12.35

Esters.

Ethyl formate	22.00	1.359	5.2	5.00
Propyl formate	22.20	1.379	7.4	4.70
Propyl acetate	22.00	1.385	5.6	4.75

Aldehyde and ketone.

Acetaldehyde	—	1.329	4.9	4.45
Methyl ethyl ketone	—	1.378	5.3	4.00

2. Influence of Greasy Contamination on Water.

As is well known from the investigations of Rayleigh, Langmuir, Adams, and others, the surface-tension of water is greatly diminished when even a very minute quantity of oily matter contaminates its surface. It appeared therefore of great interest to determine how the surface-opalescence of water is altered in such cases. It would obviously be extremely tedious and difficult to carry out experiments on the effect of greasing and re-cleansing water-surfaces *in vacuo*. Fortunately, however, it is actually possible to make observations with water-surfaces in the open. Distilled water is poured into a carefully cleaned glass dish painted dead black outside, and the surface of the liquid is cleaned by blowing off the superficial layer. Sunlight is focussed upon the clean surface of the water at about 45° , and the eye is placed so as to view the surface in a direction nearly adjacent to the reflected rays. A screen with an aperture suitably placed is found very convenient, as it cuts off the regularly reflected light and all stray illumination, the illuminated water-surface being seen through the aperture. The internal scattering in the water is considerably enhanced by the presence of motes caught by the water from the air. Nevertheless, the superficial opalescence by water clean enough to show vigorous camphor movements is readily observed with this arrangement as a greyish-white cap terminating the bluish-white internal track. Unless the air of the room is particularly free from dust, occasional dust-particles sail into view, are caught by the water surface and dragged down.

The effect of greasing the surface is readily observed; with a very minute quantity of oleic acid, so small that camphor movements are only slightly affected, nothing noticeable happens; but when the quantity is just sufficient to stop camphor movements, the surface-opalescence brightens up appreciably, and is then more easily distinguished from the internal scattering. The increase of intensity, though quite clear and definite, is not very large, say about 100 per cent. Figs. 7 and 8 in Plate 6 show the phenomenon, the former being obtained with clear water and the latter when the surface is greased in just sufficient quantity to stop camphor movements. Some dust tracks appear in the photographs, otherwise, however, the brightening of the surface-cap is evident enough on a comparison of the two pictures. (See Plate 6.)

Examined through a microscope, the greased surface showed no trace of structure, the opalescence being perfectly uniform and continuous. When, however, the oleic acid used is in excess of the minimum required to stop camphor movements, a remarkable change takes place. The opalescence of the

surface brightens up enormously, perhaps a thousand-fold. At this stage, shown in fig. 9 in Plate 6, the illuminated area on the surface is no longer continuous, as seen in a microscope, but is seen to contain an enormous number of micro-globules of oil. A micro-photograph of the surface at this stage is shown in fig. 6 in Plate 6.

The light scattered by the film often exhibits colour which is different in different directions.

The observations of surface-opalescence thus seem clearly to confirm the existence* at one stage, as contemplated by Hardy, Langmuir and Adams, of a continuous film of the oleic acid of extreme tenuity, whose surface-tension is lower than that of water and whose light-scattering power is correspondingly larger. At a later stage, however, when the oleic acid is in excess, it forms micro-globules which appear to rest on a continuous film of the acid. Sometimes both stages can co-exist at different parts of the surface, as shown by observations of the scattering. A trace of palmitic acid in the molten condition allowed to spread on water shows similar effects.

We shall, in a later paper of this series, go more fully into the question of the ellipticity of the light reflected from clean and contaminated surfaces of liquids at the Brewsterian angle, and consider its relation to the present investigation. Meanwhile, a few observations on the effect of greasy contamination on the polarisation of the light *scattered* by liquid surfaces may be noted here. As mentioned in Part II, when light is incident from above at the polarising angle on the clean surface of a liquid, the light scattered upwards is most conspicuous in the plane of incidence, and is then almost completely polarised in all directions of observation in which it can be distinguished from the internal scattering. This is also found to be true for a clean surface of water. A contaminated surface of water covered by a continuous film shows an increased scattering, which in this case seems distinctly less perfectly polarised for directions of observation nearly normal to the surface than for observation inclined to or nearly parallel to the surface. The globular film shows this effect even more prominently.

3. *Surface-Opalescence of Liquid Carbon Dioxide: Critical State Phenomena.*

As is well known, the surface-tension of a liquid diminishes continually and tends to zero as the critical temperature is approached. Carbon dioxide is a convenient illustration for which data are available from the measurements of

* In opposition to the view of Taylor ('Annales de Physique,' 1924, page 134), who studied the disintegration of oil-films on water by a less powerful method of investigation.

Verschaffelt. This substance when liquified by pressure has a surface-tension of 9.21 dynes/cm. at -24.3° , which falls to 2.90 dynes at 8.90° , to 1.82 dynes at 15.2° , and to 1 dyne at 20.9° . On plotting these values as a smooth graph and extrapolating to zero at the critical temperature 31.40° , it is seen that at 30° C. the surface tension is of the order of one-tenth dyne. At this temperature the liquid has still a density about twice as large as that of the saturated vapour above it, its refractive index being 1.145, while that of the vapour is 1.074. At 20° C. the refractive indices of the liquid and vapour respectively are 1.18 and 1.04.

It is clear from these figures that even at 20° C. we should expect liquid carbon dioxide to show a surface-opalescence some fifty or a hundred times more intense than that of clean water, and that as the temperature is raised to 30° we should expect it to increase even further. These anticipations have been tested by observation. A sealed bulb a little over 1 cm. in diameter containing pure liquid carbon dioxide prepared for a quantitative study of its internal light-scattering* was available and was used for the purpose. Its temperature was regulated and maintained constant by immersion in a water-bath. On illuminating the liquid normally by a thin pencil, the surface opalescence could be easily seen at all temperatures, and at 20° C. was certainly several times brighter than the surface-brightness of hexane under equal illumination. It brightened up notably as the temperature approached 30° C. With further increase of the temperature up to the critical point, the surface-opalescence increases in a most remarkable way and becomes an exceedingly conspicuous phenomenon.† Figs. 1, 2 and 3, Plate 6, are photographs of the track of the light within the CO_2 at temperatures of 30° , 30.35° , and 30.6° respectively. The internal scattering in the liquid and vapour and the surface-opalescence separating them are clearly seen in the photographs.

In a later paper of the series we shall offer quantitative measurements and comparison with theory of these changes in intensity. A few observations on the state of polarisation and distribution of intensity of the scattered light in different directions may be now noted. As we have already described the general character of the phenomena for ordinary liquids in some detail in Part II of the series, it is only necessary to indicate the features observed with

* 'Roy. Soc. Proc.,' A, vol. 104, p. 359 (1923).

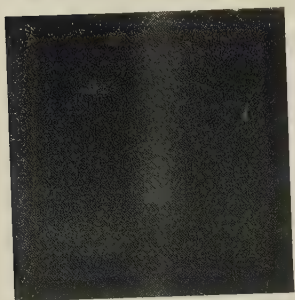
† Careful measurements recently made show that above 30.6° , the intensity of the surface-opalescence *diminishes* rapidly, the boundary between liquid and vapour becoming visibly ill-defined and ceasing to reflect light before the critical temperature is actually attained.

liquid carbon dioxide which are special for this case. The refractive index of the liquid does not differ so very much from that of the vapour above it. Consequently, the polarising angle for incidence on the liquid on either side does not differ very much from 45° , while the critical angle is much larger and approaches 90° as the temperature is gradually raised. On this account alone, we should expect the general distribution of the intensity of the scattered light as found for ordinary liquids to be somewhat modified in the case of carbon dioxide. This is actually the case. With liquid CO_2 , particularly as the critical temperature is approached, the difference in the brightness as seen from above and below the surface is not so very marked as for ordinary liquids, and the directions of maximum brightness are more nearly parallel to the surface.

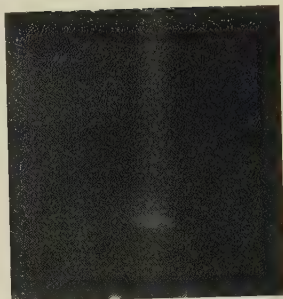
The most remarkable difference is noticed in the case in which the light is incident on the surface from above at the polarising angle. In the case of ordinary liquids, the light scattered upwards is, as nearly as can be observed, completely polarised for all directions of observation in the plane of incidence. In the case of CO_2 , however, the polarisation of the scattered light is only complete in the immediate vicinity of the regularly reflected rays and rapidly becomes imperfect as we move away from this direction on either side. The cause of this remarkable difference in behaviour must be either the small surface-tension or the small difference of refractive index of the liquid and vapour, and its complete explanation is a matter of much interest which will be taken up later on.

4. *Interfacial Scattering of Light and Critical Solution Phenomena.*

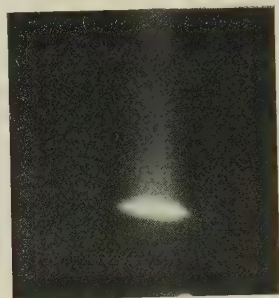
Observations have also been made by the authors of the intensity and state of polarisation of the light scattered in different directions and at different temperatures by the interface between the two layers of a mixture of carbon disulphide and methyl alcohol. Using sunlight, and suitable colour-filters, the surface-scattering can be observed over a far wider range of directions and temperatures than those found possible by Mandelstamm. The phenomena observed, and the effect of raising the temperature to the critical solution point at which the two liquids become completely soluble in each other, are very similar to those observed in the case of liquid CO_2 and its vapour as the critical temperature is approached, the layer of higher refractive index corresponding to the liquid, and the layer of lower refractive index to the vapour. Figs. 4 and 5 in Plate 6 illustrate the enormous increase in the surface-scattering which occurs as the temperature of the mixture is raised from 28° to 40°C .



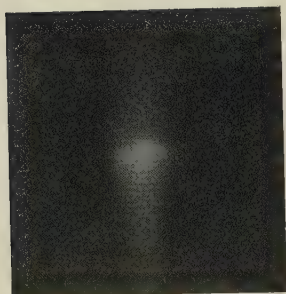
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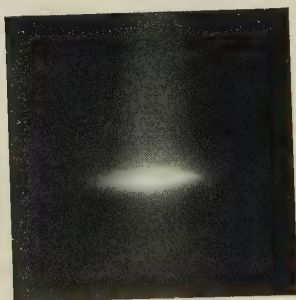
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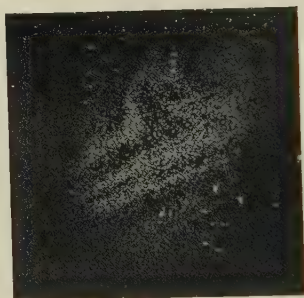
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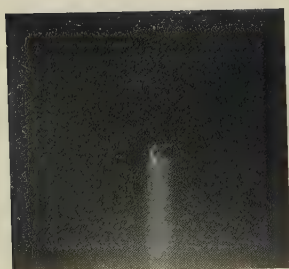
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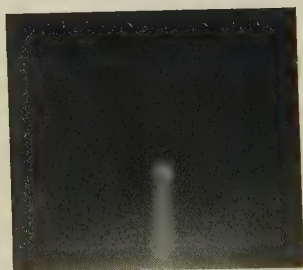
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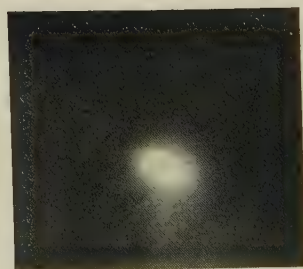
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7



8



9

(Facing p. 279.)

Quantitative measurements of this change will be presented in a later paper of the series. We shall also describe studies of the scattering of light by liquid interfaces in other binary mixtures.

Summary.

(1) Observations on the surface-scattering of light by clean water and comparisons of its brightness with those of some 28 other liquids are presented.

(2) The effect of oil-films on the surface-opalescence of water has been studied and described.

(3) The surface-opalescence of liquid carbon dioxide, its variation with temperature as the critical point is approached and the special polarisation phenomena observed in this case have been described.

(4) Similar observations have also been made of the interfacial scattering by the boundaries between the two components of a binary mixture of carbon disulphide and methyl alcohol, and the effect of raising the temperature to the critical solution point.

(5) Further quantitative studies regarding (3) and (4), observations with other binary mixtures, and theoretical discussions will be presented in the succeeding papers of this series.

DESCRIPTION OF PLATE 6.

Figs. 1, 2, and 3 illustrate the scattering by the surface of liquid carbon dioxide at 30° , $30\cdot35^\circ$ and $30\cdot6^\circ$ respectively.

Figs. 4 and 5 show the scattering by the interface of carbon disulphide and methyl alcohol at 28° and 40° respectively.

Fig. 6 is a microphotograph of the intense opalescent spot on a water surface contaminated with oleic acid when the film consists of microscopic droplets.

Figs. 7, 8 and 9 illustrate respectively the scattering by a pure water surface, a water surface covered by a film of oleic acid just sufficiently thick to stop camphor movements, and a water surface covered by a film with microscopic droplets.

Fig. 6 is a greatly enlarged picture of the effect seen in fig. 9. The few streaks in figs. 7 and 8 are due to the presence of a few dust particles on the surface, but the increased intensity of the spot in fig. 8 is clear enough.

On Atmospheric Radio-Activity and Indian Weather

By D. B. DEODHAR, M.Sc., University of Lucknow, India.

(Communicated by Prof. O. W. Richardson, F.R.S.—Received May 26, 1925.)

The pioneer observations of Elster and Geitel* have definitely shown that the atmosphere contains radio-active emanations, and that the amount of this emanation depends in some way or other upon meteorological conditions. To find an exact relationship between atmospheric radio-activity and various meteorological factors naturally becomes an important problem, since its solution is sure to offer great facilities to meteorologists in the work of accurate weather forecasting. Rutherford,† Gockel,‡ Schmidt,§ Simpson,|| Jaufmann,¶ Zlatarovič,** and others, have done much experimental work in this direction ; but from the point of view of the meteorologist, the close observations of Simpson and Gockel are specially noteworthy.

The general view held at present is that the atmospheric radium content is due to emanations from the pores of the soil ; and therefore we should expect an increase or decrease in the atmospheric radio-activity if there be an increase or decrease in these emanations. Any factor causing the pores to dilate or contract would obviously increase or lower the value of the atmospheric radium content. On the other hand, there may be factors which will cause emanations to move from one region to another ; and there may also be influences which would produce a screening effect.

The task of studying these influences and co-ordinating them is very interesting, but the influencing factors under these circumstances are so many that a large number of patient observations at various places are indispensable to form a definite opinion upon the exact relation of atmospheric radio-activity to these various factors. It is owing to these difficulties that even careful observers arrive at conflicting conclusions. For instance, Simpson†† finds that fall of the barometer is not necessarily accompanied by rise with atmospheric

* Elster and Geitel, 'Phys. Zeit.,' vol. 4, p. 526.

† Rutherford, 'Phil. Mag.,' vol. 4.

‡ Gockel, 'Phys. Zeit.,' p. 591 (1904).

§ Schmidt, 'Phys. Zeit.,' vol. 7.

|| Simpson, 'Phil. Trans.,' A, vol. 205.

¶ Jaufmann, 'Meteor. Zeit.,' 1907.

** Zlatarovič, Vienna, 'Akad. Wiss. Ber.,' vol. 129, p. 60 (1920).

†† Simpson, 'Phil. Trans.,' A, vol. 205.

radio-activity, while Gockel* concludes that radio-activity always rises with such fall. These and many other circumstances show the desirability of conducting this experimental work at as many places in the world as possible, to enable us to generalise our conclusions and to put them on a sound basis. The most favourable places for such observations would be those where the weather changes are more or less of a regular nature ; India offers this facility, and it was this that induced the author to start a series of observations, the results of which are detailed below.

Experimental.

A long bare copper wire kept insulated by means of glass rods was stretched horizontally in the open space outside the laboratory. The distance of the wire from the ground was 4 feet ; it was charged to a negative potential of 3,000 volts by means of a Wimshurst machine worked by a small motor. The potential was measured by observing the spark between two spherical conductors. A suitable induction coil with a valve rectifier was also found to work very well. The wire was kept charged and exposed for two hours and then carefully wound upon a metallic cage, which was quickly enclosed in the ionising chamber of the electrometer, and the discharge rate of the electrometer noted as usual. Schmidt's electrometer No. 241 (see fig. 1), manufactured by Messrs. Spindler and Hoyer, of Göttingen, was found very suitable for the work in hand. The leaf of the micrometer moved over a scale divided into one hundred equal parts ; the motion of the leaf and the scale divisions being observed through a microscope. The scale was calibrated, and was found to indicate 276 volts when the leaf was at zero, and 341 volts when it was at the 100th division. In almost all observations the wire was worked from 12 (noon) to 2 p.m., and the discharge rate was noted soon after detaching the wire from the machine. The electrometer was levelled and its natural leakage was measured at the beginning and end of every observation. In all cases it was found that the charged leaf would keep to a certain division for more than ten minutes, showing that the leakage was quite negligible.

As the discharge rate of the electrometer, due to the emanations deposited on the wire, depends on the time interval between the stoppage of the machine and the introduction of the cage into the ionising chamber, a stopwatch was started just when the machine was stopped and the interval noted. To drive off previous deposit the wire was dipped in dilute hydrochloric acid after each

* Gockel, 'Die Luftelektrizität.'

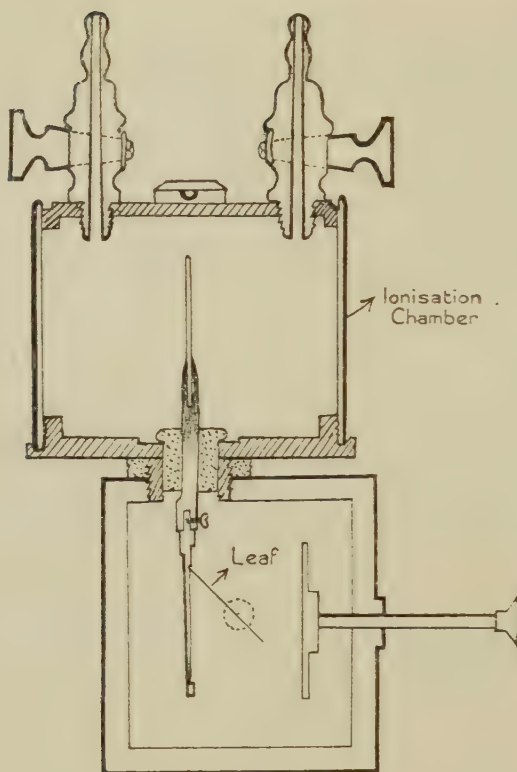


FIG. 1.

experiment and washed with distilled water. Usually the wire could be introduced into the instrument three minutes after stopping the machine. The discharge rate at various intervals was noted by calculating the time required for the electrometer leaf to travel from 100 to zero. The rate at zero time was afterwards extrapolated by plotting the various rates against the intervals. It was always found that, between the limits of intervals during which observations were made, the graph was practically a straight line. Fig. 2 will illustrate this.

The author could take only one set of observations every day, and the work extended over eight months. For the sake of comparison with the results of observations by Simpson and others, the unit of activity *A* in these experiments was kept the same: that is, when one metre of the wire discharged the electrometer one volt in one hour, the atmospheric activity *A* was said to be equal to unity. Observations were taken practically on every day of the month excepting the month of May.

For a few days experiments were made with two wires and two machines to see the effect of the variation of potential on the deposit of emanation ; and it was found that variation of voltage between 1,500 volts and 5,000 volts did not produce any change in the quantity deposited on the wire. Mund*

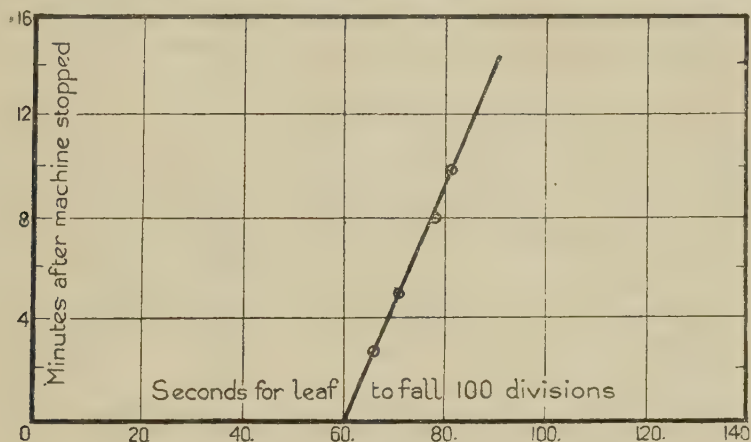


FIG. 2.

has found that the amount of activity varies with voltage, and he has given a formula in conformity with his observations. I have not met with this influence ; at any rate, within the range in which I experimented there was no such influence. In Table I, I have tabulated the mean values of the radio-activity A for different months, and it will be seen from them that, on the whole, the activity in Lucknow is far greater than that observed by Simpson and Gockel in Europe. Lucknow is very much inland and completely cut off from the influence of sea in all directions, excepting the south-east direction, but even in this case the Bay of Bengal is about 600 miles from the city. This offers a partial explanation of the high value of the radium content.

Place of observation :—Lucknow, lat., $26^{\circ} 51' N.$; long., $80^{\circ} 56' E.$; height above sea-level = 368 ft.

Table I.—Mean and Maximum Values of A in different months.

(Time : 12 noon to 2 p.m.)		
Month.	Mean Value.	Maximum Value.
October	301 ⁽⁸⁾	350
November	400 ⁽⁸⁾	412
December	412 ⁽⁸⁾	439
January	550 ⁽¹⁰⁾	600
February	521 ⁽¹²⁾	531
March	375 ⁽¹⁶⁾	400
April	322 ⁽¹⁰⁾	331
May	250 ⁽³⁾	252

* Mund, ' Jour. d. Physique et le Radium,' December, 1921.

Apart from the fact that the activity is great, the general law of its variation in the winter and summer months is practically the same as found by Simpson and others. In India the change in weather is very gradual from month to month; and so we have a corresponding regularity in the change in A. Fig. 3 shows the peak due to January, which is the coldest month of the year.

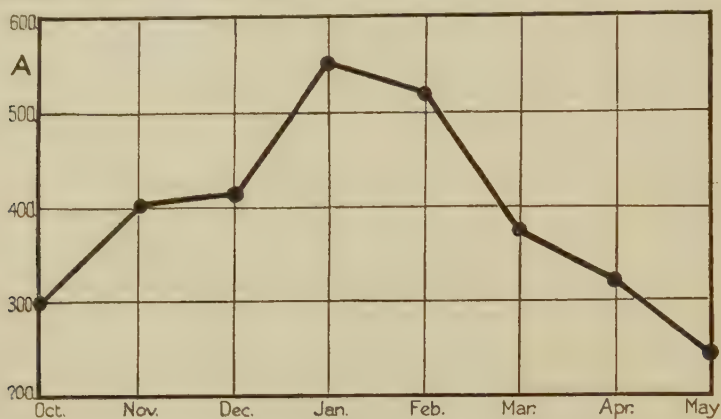


FIG. 3.

In the above table the bracketed number indicates the number of observations from which the mean value has been derived. Observations taken on very cloudy and windy days have been excluded in taking these means.

Table II shows the relation of A to barometric pressure.

Table II.—Barometer and Activity.

Month.	Barometer height, mm.	Activity.	Month.	Barometer height, mm.	Activity.
October	755	280	February	756	460
	752	300		753	500
	750	310		751	531
	754	290	March	750	380
	740	350		754	360
November.....	752	352		753	368
	752	352	April	751	381
	755	360		750	330
	750	410		752	312
December	754	400		751	314
	758	360	May	752	260
	750	430		750	271
January	750	540			
	748	580			
	751	550			

It shows that the rise in the radio-activity is as a rule accompanied by a fall of the barometer, and *vice versa*. Simpson appears to have got inconsistent results, but Gockel has found a consistent rise in the activity with the fall of pressure. In fact, I have always found that even a small change in the atmospheric pressure produces a corresponding influence on the radio-activity. This is as it should be in the light of the views put forth by Elster and Geitel.

Winds and clouds in relation to Radio-activity.

Winds seem to exert a great influence on radio-activity ; this fact has been noted by almost all observers. The natural effect of winds is to displace the emanation from one place to another, and consequently we should expect a rise in the activity if the wind brings emanation with it. On the other hand, certain winds may not bring any emanation, but remove a large portion of what is already in the region under experiment. Gockel and others find that the radio-activity is at its maximum with winds from South and West, while it is the lowest with winds from North and East. In almost all observations which I took, the result was exactly reversed. This indicates that the winds coming from the Himalayan Mountains, due North, and from Bengal, due East, bring much emanation with them. There seems to be no other explanation for this behaviour. However, a definite opinion must wait till radio-active observations in the Northern and Eastern tracts are available.

Cloudy weather always shows small radio-activity, while clear weather is attended with higher values. This effect is well known ; but the most interesting point observed by the writer is that the lowering of the activity is greater under cumulus clouds than under cirrus clouds. This fact indicates that there are some emanations coming from above, and that these are screened off by the clouds. The screening seems to be related in some way to the nature of the cloud. Is the comparatively high density of cumulus cloud responsible for the greater screening than the low density cirrus cloud ? The answer seems to be in the affirmative.

That an appreciable amount of emanation is sent out from the sun has been recently found by Bongards* ; and it further appears that the amount of emanation from the sun received by the earth should vary with the latitude, being maximum at the equator and minimum in the polar regions. This is, of course, a tentative suggestion, partly explaining a high value of radio-activity at Lucknow. It would be worth while to collect fine weather records of the atmospheric radio-activity in different latitudes, and it is proposed to take

* Bongards, ' Phys. Zeit., ' vol. 21.

observations at ten centres in India within the latitude range of 10° to 31° . On the whole, the observations during eight months of the year lend good support to the theory of atmospheric radio-activity first proposed by Elster and Geitel. Seasonal and barometric influence on the activity was remarkably consistent in these observations.

Conclusions.

1. It is found that the atmospheric radio-activity of Lucknow (India) is far greater than what is observed by Simpson, Gockel and others in Europe.
2. The rises and falls of the barometer are accompanied by systematic decrease and increase in the activity.
3. The deposit of emanation on the experimental wire is independent of potential variation between 1,500 and 5,000 volts.
4. Winds from North and East produce an increase while those from West and South produce a decrease in the activity.
5. In general, clouds produce a lowering of the activity, but cumulus produces more lowering than cirrus.
6. The observations support the theory proposed by Elster and Geitel.

The Ratio of the Specific Heats of Hydrogen.

By J. R. PARTINGTON, D.Sc., and A. B. HOWE, M.Sc.

(Communicated by Prof. H. B. DIXON, F.R.S.—Received June 4, 1925.)

The investigation of the ratio of the specific heats, $c_p/c_v = \gamma$, of hydrogen described in the present communication was undertaken during the summer of 1923 by the method previously used with air, carbon dioxide, oxygen and nitrogen.* The gas used was electrolytic hydrogen, supplied by the British Oxygen Company, and was purified in the same way as the oxygen in the previous experiments, except that the four U-tubes now contained quicklime, caustic soda, and two tubes of calcium chloride, in the order given. Phosphorus pentoxide was, as before, used for the final drying of the gas.

The globe A, fig. 1 in the paper of 1924, was, before the commencement of the experiments, filled with pure nitrogen from previous measurements. The purified hydrogen was passed directly into the globe until the nitrogen had been completely displaced, and there was thus no danger that an explosive mixture of hydrogen and oxygen could be formed, which might have been ignited by

* Partington, 'Roy. Soc. Proc.,' A, vol. 100, p. 27 (1921); Partington and Howe, *ibid.*, vol. 105, p. 225 (1924).

contact with the thin platinum wires of the bolometer, or, at least, might have formed moisture by slow reaction in contact with the platinum.

The measurements were commenced when the gas contained not more than 0·8 per cent. of nitrogen, as determined by analysis, which was made by exploding a measured volume of the gas with excess of air and finding the contraction in volume. The only alteration in the apparatus was the provision of a winch apparatus, by means of which the large stopcock could be *closed* after the expansion, whilst the galvanometer deflection was still under observation. This was necessary in order to prevent undue contamination of the gas with air on account of the rapid diffusion of the hydrogen. A series of nine values of γ' for hydrogen was obtained. No peculiarities were encountered, as compared with previous measurements, except that the period of steady deflection was shorter. As in all previous experiments, the absence of "overshooting" in the expansion was definitely proved by direct observation of the galvanometer deflections.*

The values of γ' were calculated by means of the equation

$$\gamma' = (\log p_1 - \log p_2) / [(\log p_1 - \log p_2) - (\log T_1 - \log T_2)] \quad (1)$$

Values of γ' for Hydrogen.

p_1 mm.	p_2 mm.	T_1	T_2	γ'
821·77	764·20	297·72	291·51	1·4089
819·69	762·12	298·87	292·61	1·4074
820·94	762·07	299·24	292·82	1·4113
815·40	757·50	298·33	292·01	1·4099
819·66	760·00	297·66	291·20	1·4091
818·22	760·00	297·66	291·35	1·4090
821·18	762·52	297·75	291·42	1·4083
824·67	765·40	297·70	291·33	1·4085
822·95	765·40	297·67	291·46	1·4101
.... Mean $\gamma' = 1·4092 \pm 0·0002$.				

* In connection with some criticisms of the author's previous experiments by Brinkworth ('Roy. Soc. Proc.,' A, vol. 107, p. 510 (1925)), it may be pointed out that it is quite clearly stated in the original paper ('Roy. Soc. Proc.,' A, vol. 105, p. 229 (1924)) that "no emergent stem correction was necessary, as both thermometers were completely immersed in the water of the bath," and that "in the actual experiments the thermometer was completely immersed in the water of the bath." Brinkworth is therefore in error in stating that an emergent stem correction was applied. It may also be mentioned that the presence or absence of "overshooting" could very easily be detected by the string galvanometer, and in all actual measurements in this and all previous work it was definitely proved to be absent. There does not seem to have been any obvious means of detecting "overshooting" in Brinkworth's apparatus.

This mean result now requires correction (i) for the effects of radiation, and (ii) for divergence of the gas from the ideal state, to which alone equation (1) applies.

The radiation correction for hydrogen is taken as 0.0021* and the correction for deviation from the gas laws is negligible. *The final value of $c_p/c_v = \gamma$ for hydrogen is thus 1.4113 ± 0.0002 .*

The value of $C_p - C_v$ for hydrogen is 1.9875, and hence :

$$C_v = 1.9875/0.4113 = 4.832 \text{ gm. cal.}; \quad C_p = 6.820 \text{ gm. cal.}$$

$$c_v = 2.397 \text{ gm. cal.}; \quad c_p = 3.383 \text{ gm. cal. (H}_2 = 2.016).$$

The values of γ obtained by previous experimenters were as follows : Cazin found 1.41; Dulong, 1.407; Jamin and Richard, 1.410; Masson, 1.401; but, as explained in the previous communication, no reliance can be placed on these figures. Roentgen† obtained a value 1.3852 by the adiabatic method, but Roentgen himself recognised that this was too low on account of the heat exchange occasioned by the use of too small an expansion vessel. Lummer and Pringsheim‡ found, with a larger expansion vessel, the value 1.4084. This result, which must be considered as the first of sensible accuracy obtained by this method, is probably somewhat low, for reasons which are fully discussed in a previous communication.§ It could be anticipated that Lummer and Pringsheim's value for hydrogen should be rather lower than the true value than is the case with their measurements with other gases, since in our present experiments the deflection obtained with hydrogen, although perfectly steady, never lasted more than about one second before fluctuations set in, whereas in the experiments with air, oxygen, nitrogen and carbon dioxide the steady deflection lasted for several seconds.

Shields, whose work has already been discussed,|| obtained the value 1.4012, which is considered too low for reasons previously given.

Brinkworth,¶ whose paper appeared after our experiments were completed,

* In applying the radiation correction Brinkworth follows Mercer in taking an inverse ratio of the thermal conductivities of the gases, but did not himself make any experiments to determine the radiation correction, even in the case of air. Unfortunately, the present experiments were finished, and the apparatus dismantled, before Brinkworth's paper appeared, and we were therefore unable to make the simple experiments necessary in order to test the hypothesis advanced by Brinkworth. In the meantime we apply the correction in the same way as Lummer and Pringsheim.

† 'Annalen der Physik,' vol. 148, p. 580 (1873).

‡ 'Annalen der Physik,' vol. 64, p. 553 (1898).

§ 'Roy. Soc. Proc.,' A, vol. 100, p. 27 (1921).

|| 'Roy. Soc. Proc.,' A, vol. 105, p. 226 (1924).

¶ 'Roy. Soc. Proc.,' A, vol. 107, p. 510 (1925).

finds the value $\gamma = 1.4070$ at 17°C. , but this includes a radiation correction of only 0.0004 . If the correction 0.0021 is applied, the value becomes 1.4087 , in agreement with Lummer and Pringsheim's value. The extrapolations and the corrections for the heating of the thermometer wire in Brinkworth's experiments were serious.*

Regnault† obtained a value of c_p of 3.4090 as a mean of four determinations between room temperature and 200° . This is slightly higher than the value 3.382 calculated for room temperature in the present research, as would be expected from the appreciable temperature coefficient of hydrogen. Wiedemann,‡ by a modification of Regnault's method, found $c_p = 3.410$ as the mean of two determinations between 20° and 100° , and between 20° and 200° . Joly§ determined the value of c_p directly for hydrogen by means of the steam calorimeter. The measurements were made at pressures varying from 10 to 30 atmospheres. The values are not very certain, owing to the difficulty experienced in obtaining pure specimens of the gas, and an examination of the whole set of results shows that it is difficult to derive from them any definite conclusion as to the effect of pressure on c_p . Amagat|| states that "Pour l'hydrogène, l'ensemble des résultats de M. Joly paraît indiquer pour $c[c_p]$, la pression croissant, une diminution à peine sensible." The results which Joly appears to regard as most satisfactory are the following:—

p atmospheres	..	26.412	15.876	10.396	18.82	9.66
c_p	..	2.412	2.432	2.414	2.378	2.401

In the case of other gases Joly expressed the relation between c_p and the density as a linear dependence. The last two results above then give as the

* The apparently superior sensitiveness of Brinkworth's thermometric measurements was obtained at the expense of very appreciable heating of the thermometer wire by the current. Although a relatively thick wire was used it was, in the experiments with hydrogen, heated by no less than 1.5 degrees, *i.e.*, by 15 per cent. of the total temperature change. In our experiments it would, of course, have been easy to have increased the galvanometer deflections by using stronger currents and allowing the wire to become heated. We considered it an obvious and necessary precaution to avoid such heating of the wires. It may be remarked that in the present research the greatest deviation between the individual measurements is, as before, about 0.0022 , whereas in Brinkworth's measurements it is 0.012 . Since Brinkworth states (p. 523) that "the differences between the mean and the individual values," in his experiments at room temperature, "are not greater than those found in the results of other observers," it is clear that he cannot be referring to our experiments, although this might not be obvious from the paper.

† 'Mémoires de l'Académie,' vol. 26, p. 1 (1862).

‡ 'Annalen der Physik,' vol. 157, p. 1 (1876).

§ 'Phil. Trans.,' A, vol. 182, p. 73 (1891).

|| 'Notes sur la Physique,' Paris, p. 60 (1912).

value of c_v at 1 atmosphere 2.422, at room temperature to 100°. The five results would lead to a value of about 2.42 at 1 atmosphere. The value of c_p, c_v calculated from Joly's results is about 1.410, which is in satisfactory agreement with the value found in the present research.

Lussana* measured c_p from 6 to 40 atmospheres pressure, and deduced the formula $c_p = 3.4025 + 0.013300 (p - 1)$, where p = pressure in atmospheres. This gives at 1 atmosphere $c_p = 3.4025$ gm. cal.

Eucken† determined C_v for hydrogen by enclosing the gas under pressure in a small thin-walled steel vessel and heating electrically. The volume of the vessel was 39 c.c. and when it contained 0.0966 gram molecules, corresponding with a pressure of 56 atmospheres, the value $C_v = 4.94$ gm. cal. was found, whilst for 0.1661 gram molecules, corresponding with a pressure of 95 atmospheres, Eucken found $C_v = 4.81$ gm. cal. In reducing his values to 1 atmosphere pressure Eucken makes use of a formula based on the thermodynamic relation :

$$(dc_v/dv)_t = T (d^2p/dT^2)_v, \text{ or } (dc_v/d\rho)_t = - T\rho (d^2p/dT^2), \quad (2)$$

where v = volume, ρ = density. In the case of fluids for which p is a linear function of T , c_v is independent of pressure.‡ In case van der Waals' equation applies :

$$(dp/dT)_v = R/(v - b); \quad d^2p/dT^2 = 0 \text{ and } c_v \text{ is independent of pressure.}$$

In case Berthelot's equation applies :

$$\begin{aligned} (dp/dT)_v &= R/(v - b) + a/v^2T^2 \\ (d^2p/dT^2)_v &= - 2a/v^2T^3. \end{aligned} \quad (3)$$

Now this expression is always negative, which indicates that c_v should always increase with increase of density, whereas the experiments of Joly, and the results just quoted from the experiments of Eucken himself, show that the opposite is the case for hydrogen. This discrepancy has already been pointed out by van der Waals and Kohnstamm,§ who state that the general case cannot be covered by a temperature dependence of a alone in the characteristic equation, but "only by a dependence of b as well on temperature, or on other grounds which are not taken account of in the characteristic equation (formation

* 'Nuov. Cim.,' vol. 36, p. 5 (1894).

† 'Sitzungsber. Berlin Akad.,' p. 141 (1912).

‡ Fitzgerald, 'Roy. Soc. Proc.,' vol. 42, p. 50 (1887).

§ 'Lehrbuch der Thermodynamik,' vol. 1, p. 54 (1908).

of molecular complexes, etc.).” The integration of (2) and (3), when a is expressed in terms of critical data, gives :

$$C_v^\circ = C_v - (27/32) \pi \tau^3, \quad \text{where } p/p_c = \pi \text{ and } T_c/T = \tau.$$

Eucken's two results give values of C_v° , *i.e.*, C_v at zero pressure, of 4.79 and 4.93 gm. cal. The mean of these values, which are not in very good agreement, is 4.86 gm. cal. at 0° C. The correction for 1 atmosphere pressure is negligible, hence the values at 0° C. at 1 atmosphere would be $C_v = 4.86$ gm. cal., $C_p = 6.88$ gm. cal., and $C_p/C_v = \gamma = 1.407$.

The method of calculation used by Eucken does not seem to be admissible, since his own results indicate that the value of C_v increases with fall of pressure, and the calculated value at 1 atmosphere should be larger than the experimental figures, instead of smaller. A linear extrapolation gives at 1 atmosphere $C_v = 5.11$ gm. cal., $C_p = 7.10$ gm. cal., $C_p/C_v = \gamma = 1.389$, values which are clearly not in good agreement with those found by other experimenters.

Scheel and Heuse,* using the constant flow calorimeter, found $C_p = 6.860$, which gives $C_v = 4.875$ and $C_p/C_v = \gamma = 1.407$. It has been remarked in previous communications that this particular method seems always to lead to values of γ which are somewhat too low; this is certainly the case with air, and probably with hydrogen.

Escher† found by the ordinary method $C_p = 6.898$, whence $C_p = 4.911$ and $\gamma = 1.405$ at a mean temperature of 50° C. Grüneisen and Merkel,‡ using the Thiesen resonator method, found the velocity of sound in hydrogen to be 1262.2 m./sec. at 0° C., which gives $\gamma = 1.413$. Rücker,§ from the velocity of sound, found $\gamma = 1.4053$ at 17.8° C. Trautz and Grosskinsky,|| by a complicated method, deduce a value of $C_v = 4.83$ at 22° C., which gives $\gamma = 1.412$.

The authors wish to thank the Government Grant Committee of the Royal Society for a grant which largely defrayed the expenses of the investigation, and the Council of the Chemical Society for the loan of a standard thermometer used in the experiments.

* ‘Annalen der Physik,’ vol. 37, p. 79 (1912); vol. 40, p. 473 (1913); vol. 59, p. 86 (1919).

† ‘Dissertation,’ Marburg, 1912; ‘Annalen der Physik,’ vol. 42, p. 761 (1913).

‡ ‘Annalen der Physik,’ vol. 66, p. 344 (1921).

§ ‘Annalen der Physik,’ vol. 65, p. 393 (1921).

|| ‘Annalen der Physik,’ vol. 67, p. 462 (1922).

The Osmotic Pressure of Hæmoglobin in the Absence of Salts.

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(From the Low Temperature Station, Cambridge).

Introduction.

In the general theory of hæmoglobin solutions the osmotic pressure of the pure protein does not occupy an important place, because it is simply one of many possible combinations of hæmoglobin, water, hydrogen ions, and salts. There is, however, the definite advantage in studying pure hæmoglobin solutions that, if the protein be in equilibrium with distilled water, there is no need to consider secondary complications in the distribution of salts, due to the presence of the membrane.

If a very acid protein were used, it would be necessary to consider the pressure due to hydrogen ions, but the iso-electric point of hæmoglobin is so near neutrality that the hydrogen-ion pressure is immeasurably small.

The osmotic pressure of purified hæmoglobin solutions aroused the interest of early investigators, because it offered a means of determining the molecular weight. The equivalent weight calculated from iron analyses was about 16,700, and the molecular weight must be N times as great, where N is the number of iron atoms in the molecule. According to van't Hoff's formula, the osmotic pressure should be proportional to the concentration, and if results are expressed in the form of millimetres of mercury (reduced to 0° C.) per 1 per cent. of protein, the calculated pressure is $10 \cdot 21/N$.

It is usually stated that Hüfner proved that the molecular weight of hæmoglobin was the same as the equivalent, 16,700. His results are stated below, together with the data obtained by other workers on the osmotic pressure of pure hæmoglobin.

Hüfner and Gänsser, 9.3–12.1 mm. ; Reid, 3.5–4.4 mm. ; Roaf, 5.3 mm. ; Wilson, 7–11 mm. The accepted explanation of these variable results, mainly due to Prof. A. V. Hill, is that hæmoglobin forms in pure water a uni-molecular solution, and that the lower pressures obtained by Reid and others were due to an aggregation of the molecules caused by traces of salts.

There is, however, an alternative view. Protein preparations almost always contain traces of combined acids or bases, and these diffuse away very slowly when dialysed against distilled water. It is here suggested that these impurities caused irregular osmotic effects, formerly attributed to changes in aggregation.

These two theories differ most sharply in relation to the observations of Hüfner and Gänsser. The aggregation theory rests on the assumption that theirs was the purest preparation, whilst according to the "ionic impurity" theory they obtained the largest pressure, because their solution contained the greatest concentration of impurities. It is true that Hüfner used crystallized hæmoglobin to make up his solution, but Sørensen has shown since that the crystallization of a protein does not give the pure substance, but its salt. Hüfner's material, therefore, was almost certainly impure.

It has been shown that even in the absence of proteins salts may cause large temporary pressures, lasting for 11 days, with the relatively impermeable parchment membranes (*ref.* Donnan and Harris), and for two or three days with more permeable membranes of the type used by Reid (*ref.* Reid, 1904). Hüfner and Gänsser used parchment membranes, and measured the maximum osmometer reading which occurred during the first day or two. According to my experience, the maximum pressure varied from 5 to 20 mm., according to the type of membrane used, and it bore no relation to the final osmotic pressure.

The work of Hüfner and Gänsser received popular recognition, but, in my opinion, it is not to be compared with the work of the earliest investigator, Reid,* who used a stirred osmometer with membranes more permeable by salts. Even with the improved membranes and methods described before (Adair¹), it was difficult to obtain exact equilibria with distilled water, and with the parchment system of Hüfner and Gänsser it is practically certain that the osmometer readings were not osmotic equilibria.

Osmotic Pressure and Conductivity.

The measurement of the electrical conductivity offers a method of deciding between the alternative theories, because it will show if Reid's results or Hüfner's correspond to the purest solution. The conductivity method is of great value in this problem, because the impurities are not exactly known; their concentrations may be too small for chemical analysis, and in any case ash analyses could not be used because of the risk of losing volatile impurities, such as ammonia and carbon dioxide.

The electrical conductivity of the salts of hæmoglobin is high compared with that of the pure protein, as shown in Table I. As dialysis was continued, the conductivity measurements were enormously decreased and the osmotic

* The work of Reid was discredited by Prof. Roaf on the ground that alcohol was used, but my results, obtained without the use of alcohol, agree approximately with those of Reid.

pressure tended to reach a constant steady value. The flat region of the curve is shown in fig. 1.

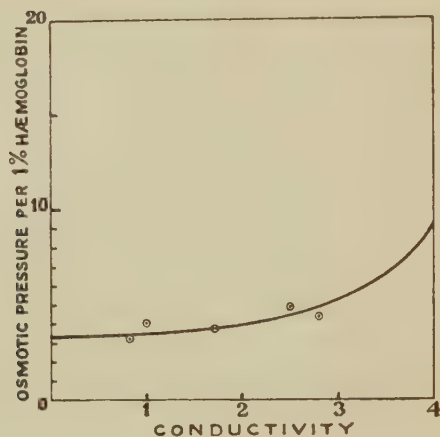


FIG. 1.

The conductivity measurements show that the degree of purity attained in these experiments was greater than that recorded by previous workers, and the character of the curve suggests that further purification would have no further effect on the osmotic pressure. The purest preparation obtained gave a pressure of 3.2 mm., which is in accordance with Reid's figures. Since the high pressures corresponding to Hüfner's value, 10.2, are correlated with high conductivities, it is probable that his results were due to undialysed acid or base.

Table I.

Osmotic pressure of purified hæmoglobin (from sheep's blood).

No. 23, sodium salt of hæmoglobin.

No. 11, 14, 13, 10, 9, dialysed hæmoglobin (8.6 grams per 100 c.c. water).

π = osmotic pressure per 1 per cent. protein, reduced to 0° C. (Experimental temp. 23° C.)

pH'' = negative log of hydrion concentration in outer liquid.

Conductivity.	pH''	π	No.
0.00092.....	11.0	21.6	23
0.00025.....	6.8	4.8	11
0.00028.....	7.0	4.4	14
0.00010.....	6.9	4.1	13
0.00017.....	6.8	3.8	10
0.00008.....	6.6	3.3	9

Osmotic Pressure and Hydrogen-ion Concentration.

At the iso-electric point of a protein, the amount of electrolyte held is a minimum, therefore the measurement of the hydrogen-ion concentration of the dialysate (initially pure water) is a useful method of estimating the degree of purification.

The results are given in Table II. It will be observed that the minimum osmotic pressure is found at the iso-electric point, as in Loeb's work, and moreover, the pressure at this point is very much smaller than 10·2. Hüfner's pressure corresponds to *pH* 5·5, and it is quite certain that acid would be bound at such hydrogen-ion concentrations. Ionizing salts of hæmoglobin would be formed which would give a much larger osmotic effect than the "partial protein pressure."

Table II.

Osmotic pressures of hæmoglobin at different hydrogen-ion concentrations.

<i>pH.</i>	π	Grams Hb per 100 c.c. solution.	<i>pH.</i>	π	Grams Hb. per 100 c.c. solution.
5·0	21·5	0·74	6·8	4·5	4·00
5·4	13·4	1·20	6·8†	6·8	0·97
6·5	3·2	1·20	7·2	5·0	1·20
6·7*	2·4	3·70	9·6	15·6	3·67
6·8	2·4	6·20	10·2	21·4	1·20
6·8	3·5	6·20			

* Iso-electric point—minimum osmotic pressure.

† Denaturation observed.

Relation between Osmotic Pressure and Hæmoglobin Concentration.

This relation offers a method of testing the aggregation theory, because polymerization ought to increase with increasing concentration. Measurements were made of the osmotic pressures of different concentrations of hæmoglobin, with distilled water for outer liquid, having a hydrogen-ion concentration about $10^{-6.7}$.

According to the aggregation theory, the pressure-concentration ratio should diminish in strong solutions, but the observed points (fig. 2) show an increase. The data contradict the aggregation theory.

The smooth curve drawn in the figure is not without interest. It is calculated from the formula

$$p = 2.55 \text{ cHb} \left(\frac{1}{1 - 0.0168 \text{ cHb}} \right) \quad (1)$$

p = osmotic pressure.

cHb = grams hæmoglobin per 100 c.c. of solvent.

Most of the observed points are higher than the theoretical curve, because it was impossible to remove all the bound electrolytes in every experiment.

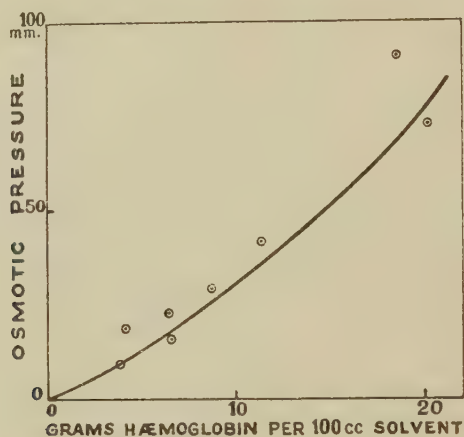


FIG. 2.

The empirical constants 1.68 and 2.55 were worked out for the pressure-concentration curve when the solvent was a mixture of chlorides and phosphates isotonic with blood. A similar curve was obtained with N/10 sodium as solvent. (Adair.²) This result is of theoretical importance, for it shows that the osmotic pressure curve is the same in the distilled water experiments as it was in the salt solutions, not only in the general form of the curve but even in the numerical values of the constants. This agreement is an additional argument against the theory that aggregation is caused by salts.

The significance of the formula will be described later in relation to the data which were used to establish it, but there are a few points which may be stated now, in order to explain the meaning of the empirical constants. In dilute solutions, the term in brackets can be neglected, and the pressure per 1 per cent. of hæmoglobin (p/cHb) = 2.55. This figure is about one-fourth of the pressure obtained by Hüfner, so it is probable that the molecular weight is four times the equivalent.

The constant 0.0168 can be explained by re-writing the formula

$$p (v - 1.68) = 255, \quad (2)$$

$v = 100/cHb$ = cubic centimetres of solvent per gram of hæmoglobin.

The term 1.68 corresponds to the "b" in van der Waal's equation, written in a simplified form below

$$p (V - b) = R.T. \quad (3)$$

Sörensen and others have suggested that the pressure of a protein should be proportional to the concentration, if the latter is expressed in grams per 100 c.c. of solvent (not solution), but this theory is not borne out by the experimental data for hæmoglobin.

Discussion of the Evidence for the Molecular Weight of Hæmoglobin.

The osmometer work described here is definite evidence against the theory that pure hæmoglobin has the molecular weight 16,700. Whether the conductivity or the hydrogen-ion concentration is used as a criterion of purity, the molecular weight is three or four times the equivalent. It is almost impossible to obtain exact results in the absence of salts, therefore the absolute value will be discussed in a later communication.

The view that the molecular weight was larger than the equivalent was advanced by Waymouth Reid, the first worker on the subject. The conclusions of Hüfner and Gänsser have already been discussed. When ionizing salts of hæmoglobin are present, the observed pressures are higher than the partial pressure due to hæmoglobin. This effect probably explains the results observed recently by Wilson (1925). Pressures are recorded which are in rough agreement with Hüfner's results, but the statement is made that: "The osmometer flask was kept loosely stoppered so that sufficient carbon dioxide entered to make the outer fluid somewhat more acid than $pH\ 7.0$."

In a paper entitled "The Nature of Oxyhæmoglobin, with a Note on its Molecular Weight," Barcroft and Hill record experiments on the heat of reaction of oxygen and hæmoglobin and the oxygen bound at different pressures. The experiments were interpreted with the aid of the equation quoted below, on the assumption that n represents the average number of iron atoms in the molecule. The authors have since pointed out that n may have other meanings (*ref.* Brown and Hill),

$$y = Kx^n/1 + Kx^n. \quad (4)$$

y = oxygen bound at pressure x , divided by oxygen bound at full saturation (oxygen capacity), x = oxygen pressure, K = constant.

Barcroft and Hill obtained the following results with their dialysed preparation :—

- (1) The oxygen dissociation curve was fitted by formula (4) when the value of n was taken to be about 1.0. The pressure of oxygen at half saturation was 8 mm.

- (2) The heat of reaction calculated by applying van't Hoff's formula was 28,000 calories. The observed heat of reaction was about 30,000 calories.

From these it was concluded that n was unity, and that therefore the molecular weight of hæmoglobin was 16,700.

This conclusion is opposed to the results of measurements of osmotic pressure, given earlier, and the observed heat of reaction has not been obtained by any later worker. The explanation of this discrepancy has been given elsewhere (*ref. Adair*³).

The exponent n was found to be equal to unity, owing to the balancing of two opposing factors—the change in acidity on oxidation which tends to give an n smaller than unity, and the fundamental form of the dissociation curve which tends to give an n larger than unity. Barcroft and Hill worked at a hydroxyl-ion concentration where the uncorrected value of n was in the region of unity.

The oxygen dissociation curves of dilute solutions of pure hæmoglobin have not been studied, but Hartridge and Roughton have developed the theory that n is unity in dilute solutions, containing salts. Unfortunately, the range of oxygen pressures which could be studied was hardly sufficient to give a decisive test. These authors, and also Adair (1925), have suggested that n need not be the same as the number of iron atoms in the molecule.

It is impossible to frame a complete theory of the reaction between oxygen and hæmoglobin, but it may be useful to prove the proposition that n may be smaller than the number of iron atoms in the molecule. The proof given below was advanced in a Fellowship Dissertation (1921), but was not published as it involved many assumptions which could not be tested. Prof. Milne has pointed out to me that similar assumptions have been made in applying the theory of detailed balancing to the ionization of atoms at high temperatures, discussed by Einstein, Klein and Rosseland and others (*ref. Milne, E. A., 'Phil. Mag.,' vol. 47, p. 209*).

Let Hgb be a molecule, which can combine with four oxygen molecules.

Let	u_0	=	concentration of Hgb.
	u_1	=	„ „ HgbO ₂ .
	u_2	=	„ „ Hgb(O ₂) ₂
	u_3	=	„ „ Hgb(O ₂) ₃
	u_4	=	„ „ Hgb(O ₂) ₄
	x	=	„ „ oxygen.

Let $\kappa, \kappa_2, \kappa_3, \kappa_4$ and $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ be reaction velocity co-efficients defined by equations 5, 6, 7 and 8.

$$\delta u_1/\delta t = 4 \cdot u_0 \kappa_1 x - 1 \cdot u_1 \lambda_1 + 2 \cdot u_2 \lambda_2 - 3 \cdot u_1 \kappa_2 x, \quad (5)$$

$$\delta u_2/\delta t = 3 \cdot u_1 \kappa_2 x - 2 \cdot u_2 \lambda_2 + 3 \cdot u_3 \lambda_3 - 2 \cdot u_2 \kappa_3 x, \quad (6)$$

$$\delta u_3/\delta t = 2 \cdot u_2 \kappa_3 x - 3 \cdot u_3 \lambda_3 + 4 \cdot u_4 \lambda_4 - 1 \cdot u_3 \kappa_4 x, \quad (7)$$

$$\delta u_4/\delta t = 1 \cdot u_3 \kappa_4 x - 4 \cdot u_4 \lambda_4. \quad (8)$$

At equilibrium, we have—

$$\delta u_1/\delta t = \delta u_2/\delta t = \delta u_3/\delta t = \delta u_4/\delta t = 0, \quad (9)$$

Let the affinity coefficients k_1, k_2, k_3, k_4 be defined by the formulæ 10, 11, 12, 13,

$$u_4/u_0 = x^4 \kappa_1 \kappa_2 \kappa_3 \kappa_4 / \lambda_1 \lambda_2 \lambda_3 \lambda_4 = \frac{1}{2 \cdot 5 \cdot 6} k_4^4 x^4, \quad (10)$$

$$u_3/u_0 = 4 x_3 \kappa_1 \kappa_2 \kappa_3 / \lambda_1 \lambda_2 \lambda_3 = \frac{4}{6 \cdot 4} k_3^3 x^3, \quad (11)$$

$$u_2/u_0 = 6 x^2 \kappa_1 \kappa_2 / \lambda_1 \lambda_2 = \frac{6}{1 \cdot 6} k_2^2 x^2, \quad (12)$$

$$u_1/u_0 = 4 x \kappa_1 / \lambda_1 = k_1 x, \quad (13)$$

Then oxygen combined at pressure x is proportional to the sum of the term

$$\frac{1}{4} u_1 + \frac{2}{4} u_2 + \frac{3}{4} u_3 + \frac{4}{4} u_4.$$

The total hæmoglobin present would be equal to $u_0 + u_1 + u_2 + u_3 + u_4$.

Let y = oxygen combined divided by total hæmoglobin. Then y is given by formula 14

$$y = \frac{\frac{1}{4} k_1 x + \frac{1}{2} \frac{6}{1 \cdot 6} k_2^2 x^2 + \frac{3}{4} \frac{4}{6 \cdot 4} k_3^3 x^3 + \frac{4}{4} \frac{1}{2 \cdot 5 \cdot 6} k_4^4 x^4}{1 + k_1 x + \frac{6}{1 \cdot 6} k_2^2 x^2 + \frac{4}{6 \cdot 4} k_3^3 x^3 + \frac{1}{2 \cdot 5 \cdot 6} k_4^4 x^4}. \quad (14)$$

If the k terms are independent of the concentrations of the components, and if all the terms except k_4 are small, the formula can be simplified: $y = Kx^4/1 + Kx^4$. Unless these conditions are fulfilled, the n calculated by Hill's method may be much smaller than the number of iron atoms in the molecule.

If the k terms are equal, the formula becomes $y = \frac{1}{4} kx/1 + \frac{1}{4} k_1 x$.

This assumption corresponds with the theory of Hartridge and Roughton. Adair,³ in collaboration with Bock and Field, suggested that k_4 might be larger than the other terms.

Summary.

The osmotic pressure determinations for dialysed hæmoglobin made by previous workers ranged from 3.5 mm. to 12.1 mm. per 1 per cent. of protein.

Variation is to be expected, for it is theoretically impossible to prepare a hæmoglobin solution absolutely free from combined acids or bases, and there is the further risk that prolonged purification may cause changes in the protein.

The theory formerly accepted was that the high pressures (about 10 mm.) represented pure hæmoglobin of molecular weight 16,700, the same as the equivalent determined by iron analyses. The lower pressures were attributed to aggregations of the molecules caused by salts.

Repetition of the work with iso-electric hæmoglobin gave pressures of 3·2 mm., or less, and pressures of 10 mm. or more were obtained only when conductivity and hydrogen-ion determinations showed that acid or base was bound.

The determinations of Hüfner (10 mm.) were made at an unknown hydrogen-ion concentration, and it is here suggested that most of the pressure in his experiments was due to undialysed acid or base. The molecular weight of pure hæmoglobin is about four times the equivalent.

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The Behaviour of Crystals and Lenses of Fats on the Surface of Water. Part I.—The Mechanism and Rate of Spreading.

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1. *Introduction.*

The phenomena to be observed when a drop of a relatively insoluble liquid is placed upon a clean surface of water, or of a metal, have been described in detail of Hardy (1), Devaux (2), and other writers.

There are two distinct ways in which spreading may occur:—

1. Vapour may distil from the drop and condense on the surrounding solid or liquid surface.

2. A film may spread out from the drop* as an expanding disc, by a process of surface solution.

Hardy (3) terms (1) primary spreading, and (2) secondary spreading. This nomenclature is open to objection, for the processes are really distinct and not consecutive. It might also lead to misconceptions as to the thickness and properties of the resultant film. We will accordingly designate (1) as “vapour spreading,” and (2) as “surface spreading.”

Hardy has shown that a pure liquid can extend on a clean solid only by means of vapour spreading. On liquid surfaces, non-volatile substances may form a film by surface spreading, while with volatile substances, one or both processes may occur.†

Either of these methods may give rise to a film unimolecular or multimolecular in thickness. For convenience one may designate the unimolecular film as the primary film. Multimolecular films may be regarded as consisting of a primary and a secondary film. Such a terminology is justified from a consideration both of the order of formation and of the marked difference in properties exhibited by the material in the primary and secondary films. The mechanism by which vapour spreading occurs is, by definition, one of great

* Or, as will be shown, from a crystalline fat.

† As we shall note, spreading is possible only when a decrease occurs in the free surface energy of the adsorbent, thus necessitating a union between adsorbent and adsorbate. Accordingly, surface spreading can take place only if the surface molecules of the adsorbent possess the mobility characteristic of the liquid state.

simplicity. We shall have occasion to discuss the conditions after equilibrium has been reached.

The process in the case of surface spreading, by which a film originating from a drop of oil, or a crystal, visibly extends over a liquid surface, and finally, after the surface has become saturated, arrives at a state of equilibrium, is highly complicated, and has received many different interpretations from the kinetic point of view. As this phenomena is closely related to and derives importance from its connection with adsorption processes in general, the experiments described in the first part of this investigation were undertaken with a view to elucidating the nature of the process. In the second part, an account will be given of the remarkable effect of elevation of temperature upon the equilibrium between a lens or a crystal of a number of surface-soluble, but bulk-insoluble, organic compounds, an effect which enables us to calculate the latent heat of fusion of the substance in question, together with the heats of surface solution of both a crystalline and a liquid lens.

2. General Theory.

In the case of insoluble long-chain fatty acids and esters upon a water surface there is no doubt, as shown by the experiments of Langmuir (4) and Adam (5), that the film is primary, or unimolecular in character. Iredale's work on the adsorption of such vapours as water, benzene, and methyl acetate on a mercury surface (6) likewise indicate that until the vapour tension becomes sensibly equal to that over the pure liquid, the film is primary. On the other hand, the films of many vapours on a glass surface, investigated by George and Evans (7) and of octyl alcohol and other volatile organic compounds on dry metal surfaces by Hardy (*loc. cit.*) are certainly multimolecular.

Hardy (*loc. cit.*), in his well-known work on lubrication, seeks to show that with the exception of practically non-volatile substances, the formation of a stable unimolecular film is highly improbable. He says: "The only condition to be satisfied by the composite is that the film should, on the average, receive in unit time as many molecules from the saturated vapour as it loses. Is it likely that a monomolecular film alone is able to fulfil this condition? It is, in my opinion, more likely that it will do so very rarely."

It does not seem that this objection is entirely valid, when we consider that the rate at which an adsorbed molecule adjusts itself on the surface, the time of molecular relaxation, is very small compared to the mean life of the molecule on the surface. Computation of the former value from measurements of thermal conductivity gives a result of the order of 10^{-12} seconds; of the latter, from the

Herz-Knudsen equation, as well as from experimental data presented in this paper, a result of the order of 10^{-7} seconds.

Further, calculations of the area occupied by each of the adsorbed molecules of pyridine at a neutral mercury—water interface, and of butyric acid at a water—benzene interface, where there is no evaporation and condensation, yield results (*see* Schofield and Rideal, p. 57, *supra*) which are identical with those obtained at a water—air interface, where evaporation and recondensation occur.

It seems plausible to assume that a unimolecular layer will result when the residual valency forces at a surface are almost entirely satisfied by the first layer formed; but whether or not this condition is reached will depend on the nature of the adsorbent, on the specific attraction between it and the given surface, and on the state of kinetic agitation of the adsorbing surface.

Measurements of the heats of adsorption of gases on metals, of vapours at low pressures on surfaces such as charcoal, and of the lowering of the surface tension of water by the addition of capillary active substances which form a unimolecular Gibbs layer, all indicate that the formation of the primary film is attended with a very great decrease of free energy of the system. The building up of secondary layers in the case of adsorption of vapour by charcoal, or of water by platinum or glass, is attended with a heat evolution which is of the order of and frequently less than the latent heat of vaporisation of the condensed vapour. Further, heterogeneous catalytic phenomena appear to be limited in all cases to the molecules adsorbed in the primary film, an indication that the forces of primary adsorption, causing deformation and possibly induced polarity of the molecules, are of a different order from the comparatively weak attractions responsible for secondary layers. In accordance with this view, there would be a sudden rise in the vapour pressure as the film changes from uni- to bimolecular depth, followed by a more gradual rise as the adsorbed layer becomes thicker, until the vapour pressure reaches that of a free surface of the liquid.

We must conclude that the residual valency forces are not in all cases satisfied by adsorption of a unimolecular film, and may adduce this as evidence either that the range of attraction exceeds the thickness of a molecule, or that induced polarity effects, as suggested above, are of considerable importance in increasing the adhesive forces represented by the “*a*” constant in the Van der Waals’ equation of state.

Unimolecular films are thus to be anticipated in those cases in which the surface of the adsorbate is not very active, *e.g.*, on diamond, or in which, in spite of a high surface activity, the specific adhesion of the adsorbate is low, *i.e.*,

the compound is characterized by a small "a" term of the Van der Waals' equation, and is far removed from its critical temperature and pressure. As an example of the predominance of the latter effect, we may cite nitrogen and hydrogen on the surface of copper. Conversely, high surface activity on the part of the adsorbent and a high specific cohesion on that of the adsorbate produce secondary films, particularly at low temperatures and high pressures. Further, the highly damped oscillations of the surface molecules of a solid (Langmuir, *loc. cit.*), in contrast to the continued reformation of surface in a liquid, may prove a factor in film stability.

3. Surface Spreading and the Equilibrium between a Lens and a Primary Film.

When a drop of non-volatile oil is placed on the surface of water it will not be, in general, in equilibrium at the moment of contact. If we designate by σ_A , σ_B , σ_{AB} , the surface tensions of the oil, water, and oil-water interfaces respectively, then according to Dupré's theorem spreading will take place if

$$\sigma_B > \sigma_A + \sigma_{AB},$$

since this would be accompanied by a decrease in the free energy of the system. Harkins (8), following Hardy (9), has made use of the magnitude of this decrease in free energy as a measure of the tendency of one liquid to spread upon another (water), and has pointed out many interesting relations between this "spreading coefficient" and the chemical constitution of the liquid A.*

The surface tension of the water will be lowered by the film of oil until σ_E is reached, when

$$\sigma_E = \sigma_A + \sigma_{AB}.\dagger$$

* It should be observed, however, that while this spreading coefficient enables us to predict whether or not a given liquid will extend on a water surface by means of surface spreading, it gives no information as to the possibility of vapour spreading. Thus a negative spreading coefficient indicates that carbon tetrachloride will not undergo surface spreading on water; but vapour spreading unquestionably takes place.

† On the assumption that water is quite insoluble in the oil. If water is slightly soluble in the oil, the surface tension of the latter sinks to a new value σ_A' , and the conditions of equilibrium are

$$\sigma_E = \sigma_A' + \sigma_{AB}.$$

We have neglected a term giving the effect of gravity in tending to spread a lens. If this is included we have as a slightly simplified form of the equation given by Hardy (*loc. cit.*)

$$\sigma_E = \sigma_A + \sigma_B - \frac{1}{2}gH^2 \frac{D_A (D_B - D_A)}{D_B}$$

in which H = thickness of lens, assumed to be flat, D_A = density of oil, D_B = density of water, g = the gravity constant.

With many substances, *e.g.*, the fats, the surface tension of the water is lowered to the equilibrium value by a unimolecular film in which the packing, or compression in the sense used by Langmuir, is not necessarily high. With substances of low capillary activity, the surface tension may be lowered to σ_E by a still closer packing, or higher surface concentration in the unimolecular film. Finally, with substances of extremely feeble capillary activity, even a highly packed unimolecular layer may fail to achieve this result. But as we have noted, further slight decrease in free energy of the surface may be achieved by secondary film formation, and such an operation may now ensue. On the unimolecular film a secondary film is formed, increasing in thickness until the value of σ_E is reached.

These conditions of equilibrium for an insoluble oil, such as oleic acid, have been investigated by Marcelin (10), while a general review of the literature and comment on numerical results is given by Carrière (11). This part of the subject will be treated more fully later.

If a drop of oleic acid is touched to a clean water surface, contained within a vessel with dry clean sides, a film is seen to spread out rapidly, the drop flattens and extends in area, suddenly breaking into a large number of smaller drops of varying size, and an instant after the film has touched the walls of the vessel, movements cease, and equilibrium is established. If the boundaries of the surface are contaminated or wet, the film will "crawl" over the further surface thus provided, and movements of the lenses will continue. Likewise, slight traces of alkali in the water delay the establishment of equilibrium.

It appeared of interest to examine how this film spreads, whether it was pulled out by clean water, or pushed out from the lens, and whether an "expanded" film behaved differently from a "condensed" film. These are questions which it has been hitherto difficult to answer because of the extremely small space of time available for observation before equilibrium is established when a liquid spreads on water.

It seemed reasonable to suppose that an oil which spreads as a liquid will not entirely lose that property when in the solid state, although we should expect the rate of spread from such a crystal to be materially less than from a lens. This we have found to be the case with a large number of substances.

If a crystal of myristic acid is placed upon a water surface previously dusted with talc, the motions of the particles indicate that a film is spreading from the crystal. After a time the surface is covered by the film, but if more talc is dusted on to the surface near the crystal, it is seen that surface solution is still taking place. These movements finally cease, indicating that an equilibrium

has been reached between the film and crystal, an equilibrium presumably similar to that between a lens and a film surrounding it.

4. *Experimental.*

The Surface Spreading of Solids.—The determination of the surface tension by the ring method appeared best adapted to follow quantitatively this process of gradual attainment of equilibrium. As ordinarily used, this method consists in determining the force necessary to pull a platinum ring through the surface whose tension is to be determined. In the present case, it is obviously desirable not to disturb the surface more than is necessary. We have, therefore, determined the force which would almost, but not quite, break the ring through the surface; and this force is directly proportional to the surface tension.

An apparatus similar in design to that described by Wolf (12), whose paper should be consulted for details of calibration, was used. A diagrammatic representation is given in fig. 1. By means of lowering the light eye-glass

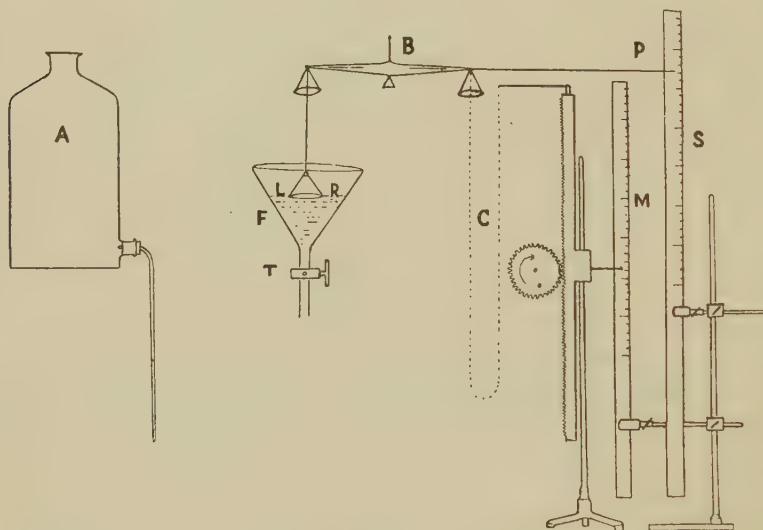


FIG. 1.

chain C, weight is gradually added to the right-hand arm of the balance B, until the movement of the pointer P on an arbitrary scale S indicates that the platinum ring R is on the verge of breaking through the surface L. The force exerted by the weight of the chain is read off on a previously calibrated scale M, and the chain is then quickly raised before the ring has broken through the surface.

In practice it was found that after the pointer P had reached a definite point on the scale, indicating that the film had been stretched to a finite distance above the surface of L, breaking always occurred if the chain was further lowered by an amount corresponding to one or two milligrams. The surface tension of the film is therefore taken as

$$\frac{\text{effective weight of chain}}{\text{corresponding wt. for pure water}} \times \text{surface tension H}_2\text{O at same temperature.}$$

In order to obtain absolutely clean surfaces, experiments were carried out on water run into the glass funnel F, through a rubber hose connected with the bottom of a tall aspirator A. The funnel was easily cleaned by filling with chromic acid solution in strong sulphuric acid. The cleaning mixture could be drained by opening the grease-free glass tap T, and the funnel washed by water from the aspirator until interference colours resulted from the draining of the water down the inside walls. A simple electrically-operated heating bath, not shown, allowed for temperature regulation.

Following Langmuir and Adam, we have worked on N/100 HCl solution throughout, as slight basicity causes soap formation, which renders results unrepeatable. It is of importance to note that clean glass dries in less than five minutes at room temperature. Films of various substances used seemed to have no tendency to crawl up the walls of the funnel when thus clean and dry.

In the determination of the rate at which a film from a crystal of a fatty substance spreads over a surface of N/100 HCl and lowers the surface tension to an equilibrium value, the procedure was as follows:—

A glass rod about 1 mm. in diameter was covered with a thick, smooth coating of, say, myristic acid, by dipping the rod into a melt of the acid, withdrawing, and allowing the acid to solidify. The weight necessary to pull the platinum ring completely through the clean surface of N/100 HCl is then determined, the position of the pointer P on the arbitrary scale being noted at the moment of breaking. The ring is again immersed in the solution, and the chain lowered until its effective weight is a few milligrams less than the actual breaking weight. By adjustment of the scale S, the pointer P is brought to zero. At this point the sensitivity of the apparatus was such that a perceptible movement of the pointer was observable for an alteration in the surface tension of the liquid of only 0.02 dynes per centimetre.

The glass rod is now lowered vertically into the surface, and a stop-watch snapped at the moment of contact. As soon as the pointer begins to move downwards, indicating a lowering of surface tension, the time is noted, and

the chain raised by an amount corresponding to several dynes. The pointer rises, but as the surface tension continues to fall the pointer gradually returns to its zero value. The effective weight of the chain and the time are again noted, and the chain again raised. In this way we obtain results of the kind shown in fig. 2.

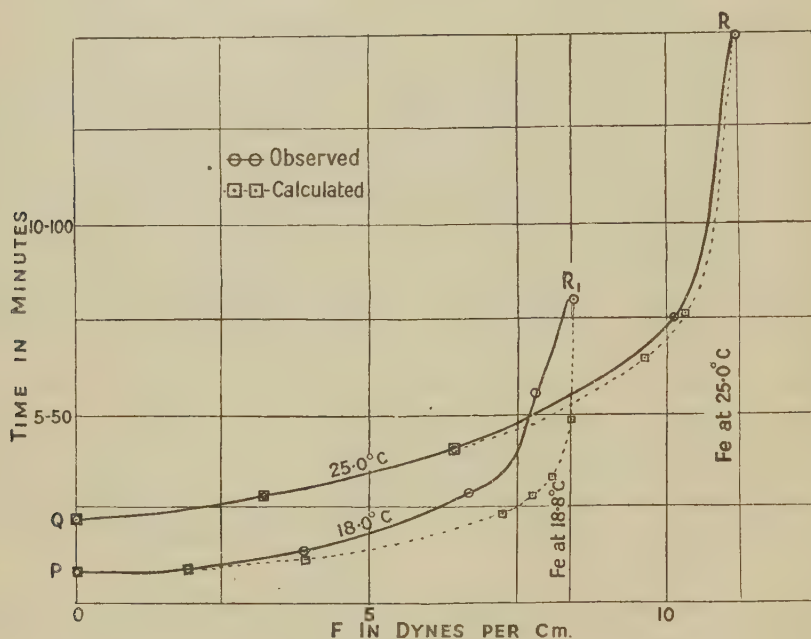


FIG. 2.

The spreading of a crystalline fat on a water surface takes place in two stages :

(a) The surface is covered with a unimolecular film under zero compression, as represented by the sections OP, OQ of the curves in fig. 2. Table I shows that for a crystal of constant circumference the time required for this part of the process is proportional to the area of the N/100 HCl surface covered. [This time is independent of the distance of the crystal from the platinum ring.]

Table I.—Myristic acid crystal at 25° C. : time for first movement of pointer P.

Area of surface in sq. cms.	Time, Mins.	Sq. cms. covered. per min.	Mean.
56.9	2.20	25.9	} 27.2
36.4	1.28	28.7	

Surface solution takes place only from that portion of the crystal in contact with the water *surface*, being independent of the depth to which the glass rod covered with acid is immersed in the water.

From the Force-Area curves for myristic acid given by Adam (13), it would appear that the area per molecule when the point Q is reached (when lowering of the surface tension begins) is about 50 A.U. Using this figure, we can calculate the rate at which the acid molecules leave the crystal. For a crystal 2.51 mm. in circumference, this rate is 9.06×10^{13} molecules per sec. at 25°C ., or 36.2×10^{13} molecules per sec., per cm. of length of the crystal face. Assuming the cross-section of a molecule in the crystal surface to be circular, and sensibly the same in area as that in a close-packed film on water, namely, 21 A.U., the number of molecules per cm. of length of crystal face is 2.2×10^7 and hence the average life of a molecule on the crystal surface is 0.60×10^{-7} secs.

(b) The packing of this expanded film, along QR, with consequent increase in two-dimensional pressure until equilibrium between surface solution and recondensation occurs. For myristic acid above 25°C . this pressure is found to obey with accuracy a unimolecular equation of the form

$$\frac{dF}{dt} = K (F_E - F_t) \quad \text{or} \quad K = \frac{1}{t} \log \frac{F_E}{F_E - F_t},$$

in which K is a constant, F_E is the force or two-dimensional pressure at equilibrium, and F_t the force at any time t .

It can be easily shown that this equation follows directly from the assumption that the rate of surface solution is constant during the whole time of the attainment of equilibrium, that the rate of re-condensation is proportional to the surface pressure F , and that this force is proportional to the number of molecules in the surface in excess of the number N_0 required to pack the surface with a unimolecular layer under zero compression. That is, $F = k(N - N_0)$, where N is the total number of molecules present at any time.

If A is the area of the entire surface, then

$$N = \frac{A}{a}, \quad N_0 = \frac{A}{a_0},$$

where a and a_0 are the areas per molecule occupied under a force of F and $F = 0$ respectively.

$$\text{Thus, we obtain } F = k' \left(\frac{1}{a} - \frac{1}{a_0} \right)$$

as the equation of state for an expanded film.

In Table II are given the observed and calculated values obtained from two typical determinations, made with the same rod of myristic acid, 2.51 mms. in circumference, on a solution of N/100 HCl. It will be seen that at 25° C. the agreement is good. At 18.8° C. there is a divergence above a force of 4 dynes per cm., the reaction being completed much more slowly than the equation predicts.

Table II.—Rate of Saturation of N/100 HCl surface by Myristic Acid Crystal, 0.251 cms. in circumference.

Observed and Calculated Values of Time for Tension to fall F dynes.

T = 18.8° C.			T = 25.0° C.		
$k = \frac{1}{t} \log_{10} \frac{F_E}{F_E - F_t} = 0.051.$			$k = 0.197$		
F in Dynes.	t obs. in mins.	t calc. in mins.	F in Dynes.	t obs. in mins.	t calc. in mins.
0.0	7.90	—	0.0	2.05	—
1.90	9.70	10.08	3.22	2.85	2.81
3.80	12.32	13.02	6.44	4.00	3.95
7.18	34.40	24.10	9.65	6.80	6.50
—	—	—	10.31	8.10	7.76

A comparison with N. K. Adam's (*loc. cit.*) F-A diagrams for myristic acid, at temperatures from 3.5° to about 30° C., shows that above 25° C. the film is expanded even under equilibrium pressure, while at temperatures below 20° C., the film would pass from the expanded to the condensed state during its progress towards equilibrium. It is obvious that the two-dimensional equation of state given above could not be expected to hold for condensed films, inasmuch as there is no term present to allow for the mutual attraction or adhesion in the film, the influence of which factors we are at present unable to evaluate, as Adam points out (*loc. cit.*).

That this equation does hold for expanded films, however, indicates that for long-chain substances there is a limit at ordinary temperatures to the expansibility of a film, that is to say, the molecules are unable to separate completely on the surface, but are held together more or less firmly (depending on the length of the chain and the temperature) by the attraction of the hydrocarbon chains for each other. The same idea is expressed if we say that every molecular collision occurring on the surface is inelastic.

Marcelin (*loc. cit.*), in making force-area determinations with oleic acid films, mentions F values observed of the order of 0.01 dynes, and concludes that the analogy of a gas holds for expanded films down to negligible compressions. From these experiments, however, it would appear that in this respect the original theory of a limit to the possible extension of a film is correct. The extremely low value of F observed by Marcelin may have been due to a repulsion operating between the floating and stationary barrier which we have observed when working with an apparatus of the Langmuir type, which in the case of paraffined surfaces may introduce a considerable correction to the observed values of F , particularly when float and barrier are only a few centimetres apart.

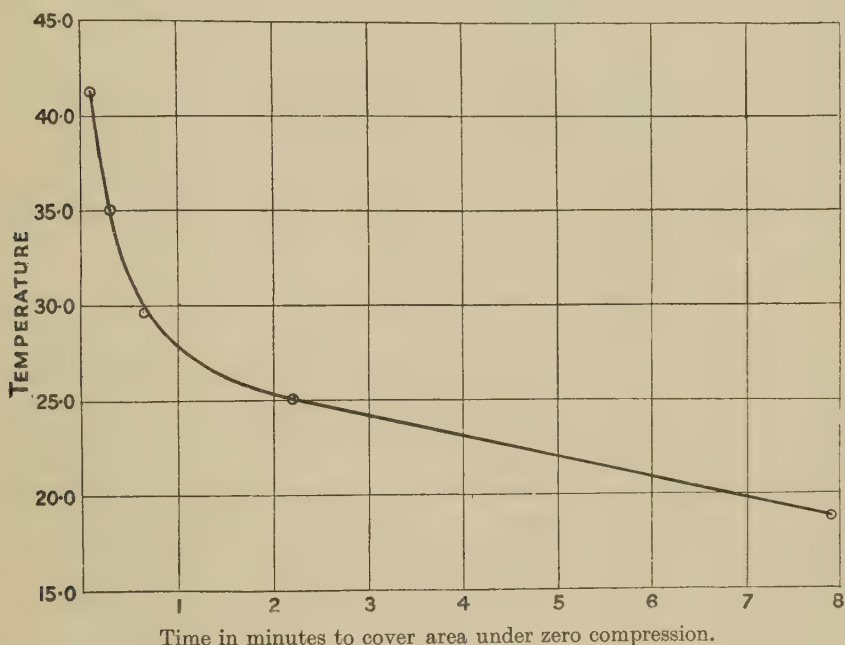


FIG. 3.

Fig. 3 gives the effect of temperature upon the time taken to reach the point O for an $N/100$ HCl surface of 56.9 sq. cms., the same rod of myristic acid being used for all four points. In order to observe any possible change in the circumference of the rod due to solubility, the experiment at 18.8°C. was repeated after the reading for 41.4°C. had been taken. The time agreed within a few seconds. The values given in fig. 3 are, however, not of the same order of accuracy as those in fig. 2, as the experimental difficulty at high temperatures is considerably greater, and the time for observation extremely short.

The curve appears to approach an asymptote parallel to the temperature axis. This form of measurement is not accurate above the temperatures indicated, but it may well be that a limiting value is reached at the melting point. Now there can be no doubt that the film spreading from the crystal is unimolecular. After melting, the only change in the spreading process is that molecules leave a liquid-liquid rather than a solid-liquid interface; and since, as we shall show later, the equilibrium pressure does not alter discontinuously at the melting point, there is every reason for assuming that the film which spreads after melting is also entirely unimolecular in character.

The experiments described above for myristic acid have been repeated qualitatively for the following substances:—

The straight-chain acids from C 11 to C 18.
Methyl, ethyl, propyl and butyl palmitates.
Hexadecyl and octadecyl acetates.
Hexadecyl and octadecyl ethers.
Palmito-nitrile.
Octadecyl phenol.
Hexadecyl urea.

The same type of phenomena occurs in every case, but the rate of spreading and the time taken to attain equilibrium vary enormously, and may require as long as twenty-four hours in the case of stearic acid at room temperatures, which appears to spread as a condensed film. The variation of the equilibrium *F* value with chemical constitution and with alteration of temperature is discussed in Part II of this investigation.

The Surface Spreading of Liquids.—Brinkmann (14) has given some experimental evidence on this question. His object was to compare the rate of extension of an oil film with that of the propagation of a nervous impulse. His measurements were made by dropping a known volume of oil at one end of a surface of water contained in a rectangular trough 125 cms. $\times$ 2 cms., and noting the elapsed time when the surface tension at the other end had fallen by two dynes, as indicated by the breaking through the surface of a platinum ring, suitably balanced. He found values of the order of 25 cms. per sec. for oils, such as oleic, propionic, and caproic acids. The water surface was then covered with a low-boiling paraffin, and the experiments repeated, the oil being injected at the interface paraffin-water. The observed times remained unaltered. Since nervous impulses are known to travel at a rate of about 60 metres per sec.,

he concluded that the spread of some substances over an interface in the tissue could not provide a mechanism.

A preliminary examination of the rate of spread of oleic acid on the surface of water contained in long horizontal glass tubes, the interiors of which were freshly coated with pure paraffin wax for each experiment for the purpose of confining spreading to a limited surface, made evident the fact that such rate of spread is higher the smaller the tube diameter, and that the velocity of the advancing film falls off with its distance from the point at which the surface was inoculated with oil. No attempt at careful quantitative determinations was made with this method, but in general the values were less than those obtained by Brinkmann, whose water surfaces may not have been free from contamination.

It is clear that the spreading film on reaching the sides of the tube undergoes compression, with consequent alteration in velocity. To determine the true rate of spread under free expansion, a large area of water surface is evidently required. Such a surface, easily cleaned, is provided by the simple arrangement shown in section in fig. 4, of a large circular galvanized-iron tank, from the

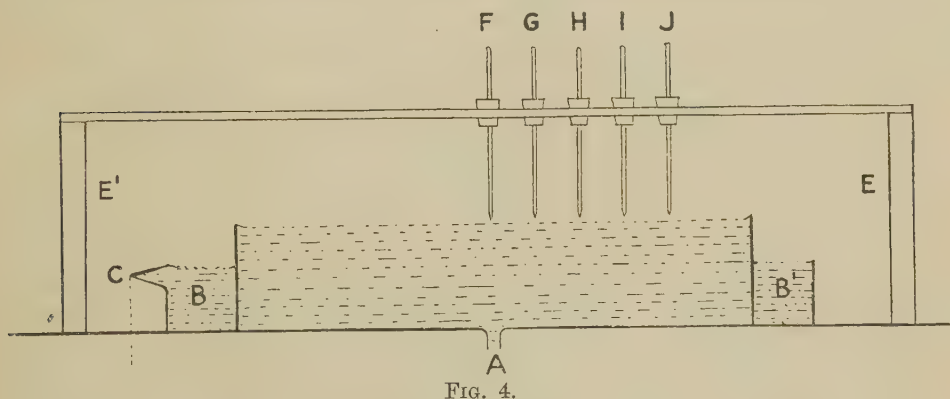


FIG. 4.

bottom of which tap-water enters at A, and overflows into the surrounding trough B, B', drained in turn by the spout C. A wooden bar D, supported over the tank by uprights E, E', is pierced at 10-c.c. intervals by inch holes, which are plugged by corks supporting small glass rods G, H, I, J. These rods terminate a few millimetres above the surface. The rod F in the centre hole fits loosely in its cork; after the end has been dipped in oil, it can be pushed down until it touches the surface, which is thus inoculated. After washing for 15 minutes, a perfectly clean surface results.

The water is made, roughly, N/100 HCl by the addition of concentrated

HCl from a pipette. As soon as surface agitation has subsided, freshly ignited talc is dusted on to the surface, the rod J is depressed, and the time taken for the edge of the spreading circle of oil, as defined by the talc swept back before it, to reach the points F, G, H, I is noted.

Typical distance-curves for oleic acid are shown in fig. 5. Curve A is that

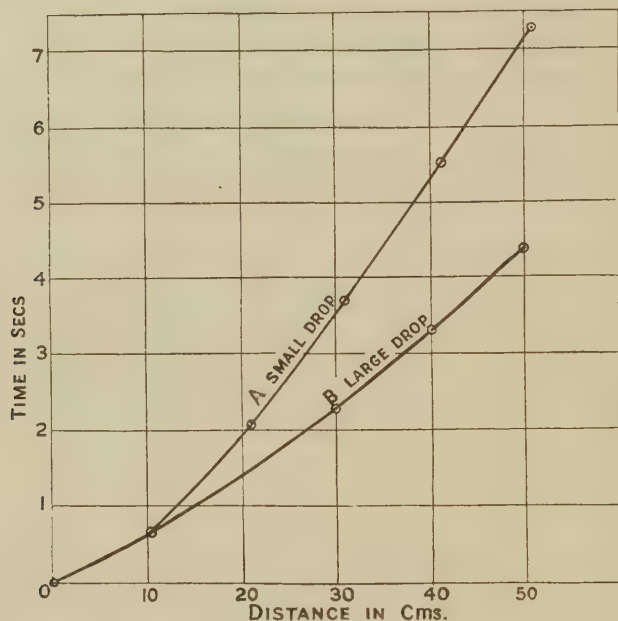


FIG. 5.

obtained when the surface is inoculated with a large drop of oil of approximately 0.1 c.c. volume; curve B results when a lesser amount of oil is used. No attempt was made to determine the exact amount of oil in any case.

It is seen at once that the rate of spread is dependent on the amount of oil used for inoculation. This is true for other oils used—namely, ricinolic and caprylic acids, which give very similar values. Further, in any given experiment, regardless of the absolute velocity of the advancing film of oil, there is a comparatively rapid extension for the first few centimetres, beyond which the velocity is constant, over the range measured.

That this velocity should be dependent on the size of the oil dose is not surprising. In the case of a crystal, we saw that surface solution occurred only from where the water surface touched the crystal, and not at the interface water-crystal. Thus, it is probable that when the source of oil molecules is a liquid lens, solution occurs only from its circumference, and the rate of formation

of the film would be proportional to this circumference, and hence to the amount of oil put on.

The attainment of a constant velocity is not in agreement with what might first have been anticipated from the behaviour of a crystal, in which the film advanced at a rate inversely proportional to the square of the radius of the area already covered. But, whereas a crystal remains sensibly constant in circumference during an experiment, a lens begins to split up into any number of smaller particles, which are in turn subdivided and swept out over the surface by the advancing film. Although the total *interface* would hardly be changed in area by this process, the total circumference of a number of small lenses would be much greater than that of one large lens. This would account qualitatively for a deviation from the inverse-square relationship. The attainment of what appears to be a *constant* velocity over the comparatively small range available for investigation, may be entirely fortuitous, and, in all probability, extended measurements would show a gradual fall in this velocity as the area grew increasingly large in relation to the amount of oil put on the surface at the start.

From the experiments with crystals, we have come to regard the film as being *pushed out* from its source, in direct opposition to the view of a *pulling* action being exerted by the water just in front of the film at any moment. With the crystal this process is so slow that no effect of viscosity, or friction between the film and the underlying water, is observed; that is to say, there is no back pressure exerted by the film on the crystal until the entire surface is covered, and close-packing can begin. When the film spreads with the extreme rapidity characteristic of a liquid oil, however, some such effect might be anticipated, resulting in a kind of two-dimensional pressure gradient, highest near the source from which spreading occurs, and decreasing as we approach the advancing boundary of the film. In terms of surface tension, the tension near a lens would be low, that at the outer edge of the film sensibly that of water while the spreading process was taking place.

Experiment shows this to be the case. The platinum ring is suspended from a balance mounted over the circular trough, and immersed at a distance of 30 cms. from the centre, F. Weights are applied to the right-hand pan of the balance until we are within a few milligrams of the breaking weight for pure N/100 HCl. The surface is inoculated with a drop of oleic acid at F. If the surface is absolutely clean, the film may sometimes pass 5 cms. beyond the point at which the ring is suspended before breaking occurs, viz., before the tension in the advancing outer edge of the film has fallen as much as a tenth of a dyne.

The surface is cleaned and the experiment repeated, with the difference that the ring is adjusted so as to break through the surface when the tension has fallen by, say, 5 dynes below that of pure water. The advancing film will now pass perhaps 15 cm. beyond the platinum ring before breaking occurs.

Unfortunately, the results of these observations cannot be duplicated quantitatively, for the reason that a large lens begins to split up into smaller drops the moment it is placed upon the surface. These movements are highly irregular, so that it is not possible to measure accurately the distance of the platinum ring from the nearest small lens at the moment of breaking through the surface. We have, however, definitely established the fact that a pressure gradient does exist, the surface pressure rising from less than a small fraction of a dyne, at the film's outer edge, to approximately 70 per cent. of the equilibrium value, close to a lens which is surrounded by a spreading film 20 cm. in radius.

We must conclude that the outer advancing edge of the film is in a condition of maximum extension, and that it is being pushed out by the entry into the surface of additional oil molecules at the circumference of each lens. In the existence of this pressure gradient we find an obvious explanation of the effect of decreasing diameter on the rate of spread in tubes.

Purity of Materials.

The water used to make up N/100 HCl solutions was generally distilled from and condensed in copper. Identical results were obtained with water distilled from silver and condensed in silica. Care was taken to avoid contact with taps that had been greased.

The experiments were carried out in a room far removed from any organic preparation work, and the air was comparatively free from dust and contamination. Cambridge tap-water appears to be entirely free from oily suspended organic matter.

With the exception of oleic, ricinolic and caprylic acids, all the long-chain compounds used were samples of the preparations of N. K. Adams (*loc. cit.*) of exceptional purity, as shown by his results with the same. Kahlbaum's "K" oleic acid was used, melting point 6-7° C. The ricinolic and caprylic acid were Poulenc Frères' preparations, and were both clear liquids.

Impure materials are easily recognized in these experiments, as pure compounds gave equilibrium "F" values independent of the amount of compound on the surface. A half-dozen so-called "pure" acids of well-known chemical

houses gave equilibrium "F" values which fell steadily with fresh additions of material.

Summary.

1. In an experimental study of the process of "surface spreading" on water and solutions of N/100 HCl of organic compounds containing a long chain terminating in a polar group, including acids, esters, ethers, phenols, and nitriles, it is found that unimolecular films spread from crystals as well as lenses, a definite equilibrium surface tension or two-dimensional pressure characteristic of the substance in question being established.

2. Methods are described by which the rate of spread and subsequent establishment of equilibrium may be followed,

3. A limit is established to the extension of expanded films, and a theory postulating inelastic collisions of molecules in the surface is advanced to account for the phenomena.

4. Spreading oil films appear to be pushed out from the source (lens or crystal) by the further entry of molecules into the surface layer rather than pulled over a surface by the attraction of the uncontaminated water.

5. It is possible to calculate from the experimental results the mean life of a molecule on the surface of a crystal in contact with water.

We wish to express our appreciation of the kindness of Mr. N. K. Adam in making available his valuable collection of long-chain preparations, without which the investigation could not have been completed; of Dr. C. Wolf for particulars of the chainematic balance employed; and of Messrs. Brunner, Mond, for a grant from which the necessary platinum rings were purchased.

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The Behaviour of Crystals and Lenses of Fats on the Surface of Water.—Part II. The Effect of Temperature on the Equilibrium Pressure.

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In Part I a study was made of the rate of spread and unimolecular nature of films of fatty substances, containing a long hydrocarbon chain and a polar "head," over a surface of pure water or of N/100 HCl. It was shown that after a definite interval of time, the surface became saturated with a unimolecular film in equilibrium with either a crystal or a lens of the substance in question, and that the time taken to attain equilibrium as well as the equilibrium surface tension was a function of the temperature.

In the present paper the effect of increasing temperature on the two-dimensional equilibrium pressure is considered in detail.

1. *Experimental.*

With slight variations, the method was that described in Part I above. Since the equilibrium pressure is independent of the absolute amount of pure fat on the surface, in the present experiments a few crystals were placed on the N/100 HCl by touching the surface with a clean moist glass rod, to which some of the powdered fat adhered, and the rod withdrawn. The movements of these crystals could be observed with a microscope.

Temperature regulation was obtained by immersing the funnel in a thermostat. To prevent the condensation of vapour on the chainematic balance used to determine the force necessary to pull a platinum ring through the surface, the balance was protected by an asbestos sheet placed horizontally between it and the funnel and thermostat. The point of zero balance was frequently checked while working at high temperatures, but the error due to air currents and condensation of moisture on the balance never exceeded 0.1 dynes. Equilibrium was considered as having been reached when no further change in surface tension occurred. After the crystal had melted, equilibrium was established practically instantaneously.

With crystals as the source of the film, long-chain acids may require as much as 48 hours at low temperatures; but most of the substances examined gave no alteration in the surface tension two or three hours after the surface had been

inoculated. During prolonged experiments a large, clean filter paper, with a narrow slit running from the edge to the centre to allow for passage of the wire supporting the ring, may be laid over the funnel to prevent contamination from the air. When the film is solid, the ring must be left in contact with the solution some hours before a reading is taken. With liquid films this is of less importance.

In these experiments, the ring was pulled completely through the surface by very gradually increasing the weight on the right-hand arm of the balance. The absolute value of the surface tension obtained depends somewhat on the rate at which the weight is increased; but if the chain is always lowered at the same rate of speed, which is easily accomplished after a little practice, values checking to 0.1 dynes are obtained, and hence *changes* in surface tension are accurately determined, although the absolute values may be as much as 0.5 dynes out. This lack of absolute accuracy in the present determinations is justified by the fact that it was necessary to take many hundreds of readings, and that we are concerned only with the change which rising temperature produces.

At high temperatures a simple siphon arrangement automatically adds distilled water to the N/100 HCl solution in the funnel to make up for that lost by evaporation, and thus ensures a constant level and area of surface.

The unquestioned purity of all the compounds used, with the possible exception of oleic acid, was discussed at length in Part I. The oleic acid was Kahlbaum, "K" quality, and melted fairly sharply at 6–7° C. In general, the test of purity used is that the equilibrium pressure is independent of the absolute amount of the crystalline or liquid fat with which the surface is inoculated.

Ordinary so-called "pure" fatty acids as supplied by the leading chemical houses, are all highly impure by this test. In some cases, however, it was found possible to obtain entirely satisfactory results with these preparations by refluxing for some days the melted oil floating on about a litre of N/100 HCl, the solution being slowly but continuously renewed. It would appear that most of the impurity in these preparations is comparatively much more soluble than the long-chain fatty acids. N/100 HCl entirely free from oily matter must be used in this purification, the acidity preventing the possibility of any soap formation.

2. The Fatty Acids.

Fig. 1 gives the surface tension of N/100 HCl when the surface is saturated with a film in equilibrium with the acids in bulk, at various temperatures.

The curve for the surface tension of pure N/100 HCl is included for reference. It is sensibly the same as that of water. The difference between the tension in the saturated surface and that of N/100 HCl at the same temperature, may be considered as analogous to the compression or "F" of the film, as determined directly by Langmuir (1) and Adam (2), and will be denoted by F_e .

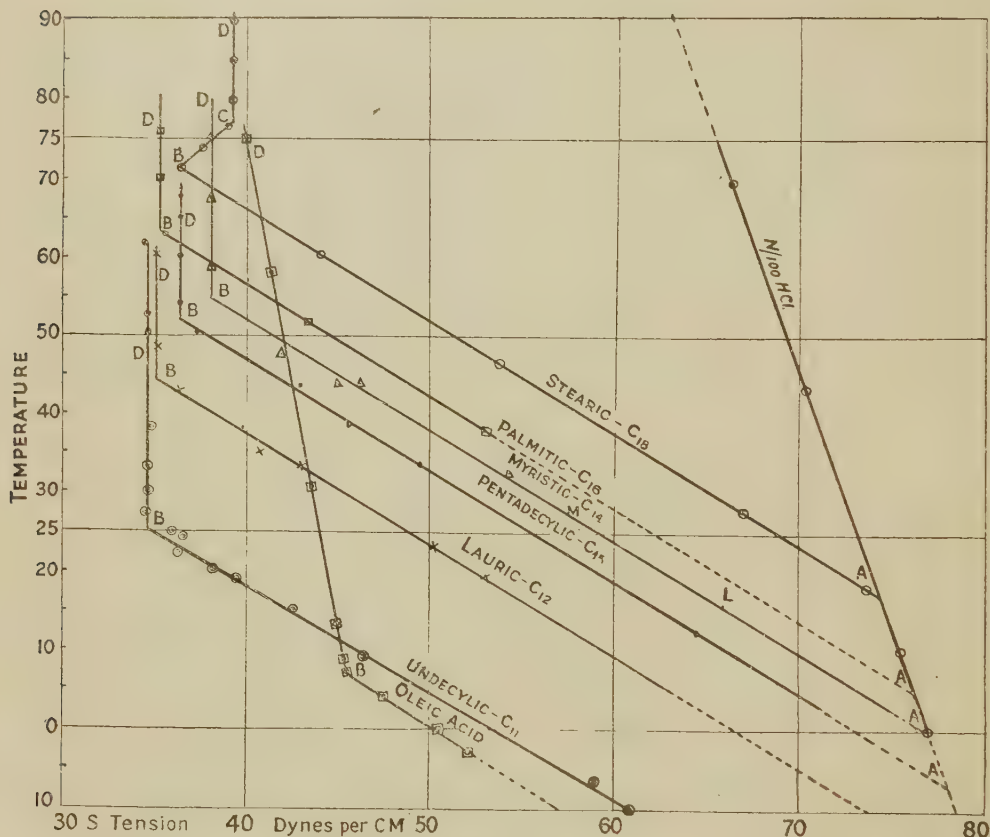


Fig. 1.

We may note the following :—

(a) When working with highly insoluble compounds, below a definite temperature A, there is no surface solution which we have been able to measure ; that is to say, a crystal of pure stearic acid, for example, will remain floating on a surface of N/100 HCl at 16° C. for an indefinite time without causing any lowering in surface tension. We may imagine (see Part I, p. 301, etc., above) that a molecule of stearic acid may be torn off the crystal by the attraction of the water for its carboxyl group only when the amplitude of vibration of

molecules in the crystal surface is sufficiently great to overcome the forces responsible for crystallisation.

(b) Above the temperature of A, surface solution occurs from the crystal, and the surface tension is lowered linearly with increasing temperature until the point B is reached, at which the crystalline acid melts. The slope of A B is sensibly the same for every compound studied, including saturated and unsaturated acids, esters, phenols, ethers, nitriles and ureas. The curve for stearic acid beyond B shows that the surface tension begins to rise in a linear manner with increasing temperature. At C there is a further change in direction for this compound, such that along C D there is practically no change in surface tension with increasing temperature. For the other acids the portion of the curve B C is missing, the lines B D corresponding to C D for stearic acid.

(c) In general, the shorter the chain the lower the surface tension for any given temperature; but an acid with an odd number of carbon atoms lowers the surface tension more at a given temperature than the even acid with one less carbon atom. In this respect the surface tensions are in the same order as the melting points.

These observations throw light on the stability of unimolecular films in general. A sharp distinction must be made between films in equilibrium with a lens or a crystal (films which have spontaneously spread from either of these sources and finally attained an equilibrium pressure) and those systems consisting of a film spread on a water surface with the aid of some solvent, the solvent later evaporating and leaving the surface covered with a unimolecular layer, as studied by Devaux (3), Langmuir (*loc. cit.*), Adam (*loc. cit.*), and others. It will be shown that the former process is reversible, and that a perfectly stable condition of equilibrium is reached if sufficient time be allowed. The latter type of film may be either stable or unstable, depending only on the temperature and pressure.

We may take the example of stearic acid, which spreads spontaneously from a crystal at temperatures above 17° C., the point A, fig. 1. Although it is possible to form a film of this compound with the aid of a solvent at temperatures below 17° C., the resulting system is theoretically unstable, regardless of the compression to which it is subjected. That it does not spontaneously contract is due to two causes; first, that there are no crystalline nuclei upon which condensation could take place, and second, that even were a crystal present, attainment of equilibrium at low pressures and temperatures is an extremely slow process. If the temperature of such a film is now raised above

17° C., it is stable at all pressures up to and including F_c at the new temperature, but unstable beyond the latter pressure.

According to these views, the "collapse" which always occurs with films, as studied by Langmuir (*loc. cit.*), takes place when the compressional force has become so great that the already unstable film breaks down upon the formation of the first crystalline nuclei. Obviously the appearance of such nuclei will seem to be more or less fortuitous, depending on such factors as the presence of dust particles in the film; and the compression at which collapse takes place may never be exactly the same in two experiments, as is found to be the case in the laboratory.

Adam (*loc. cit.*) found that a film of a very long chain substance, such as cerotic acid, with 22 carbon atoms, could be spread by the aid of solvents, but that the film contracted spontaneously without any application of pressure. If the temperature were then sufficiently raised, a stable film resulted. The "A" temperature of this compound would be extremely high. The film as first formed would accordingly be theoretically unstable; but in this case the magnitude of the lateral attractions of the long hydrocarbon chains, as Adam pointed out, would be sufficient to cause the spontaneous formation of nuclei, and the film would contract. When the temperature is elevated above that of the point "A," the film becomes stable, and withstands considerable lateral compression.

The lack of mobility characteristic of the solid state would favour the continuance of unstable films at pressures above F_c . There is experimental evidence that when F_c is exceeded for liquid films, lenses appear, and further compression serves to force the film into these lenses.

Both Langmuir and Adam observed that a solid collapsed film would not spread spontaneously, although some of their experiments were carried out at temperatures at which, according to our measurements, a film would spread from a crystal of the substance in question. It is possible that in no case did either of these investigators allow a sufficient lapse of time for spreading of the type studied in this paper to take place. There is, however, the interesting possibility that collapsed film is not crystalline in structure. If the polar groups on being forced out of the water by high tangential pressure entrain a certain amount of the water, the water-seeking tendency of this portion of the molecule would be partly, if not wholly, satisfied in the collapsed film, with the result that there would be little or no tendency for further spreading to occur. In this event we should probably regard collapsed film as a condition corresponding either to that obtaining in soap films, or the inverse of a soap micelle.

3. The Esters.

Fig. 2 gives the F_c values for the esters octadecyl and hexadecyl acetates, and ethyl palmitate, at various temperatures. In general these substances behave like stearic acid, although the temperature at which surface solution

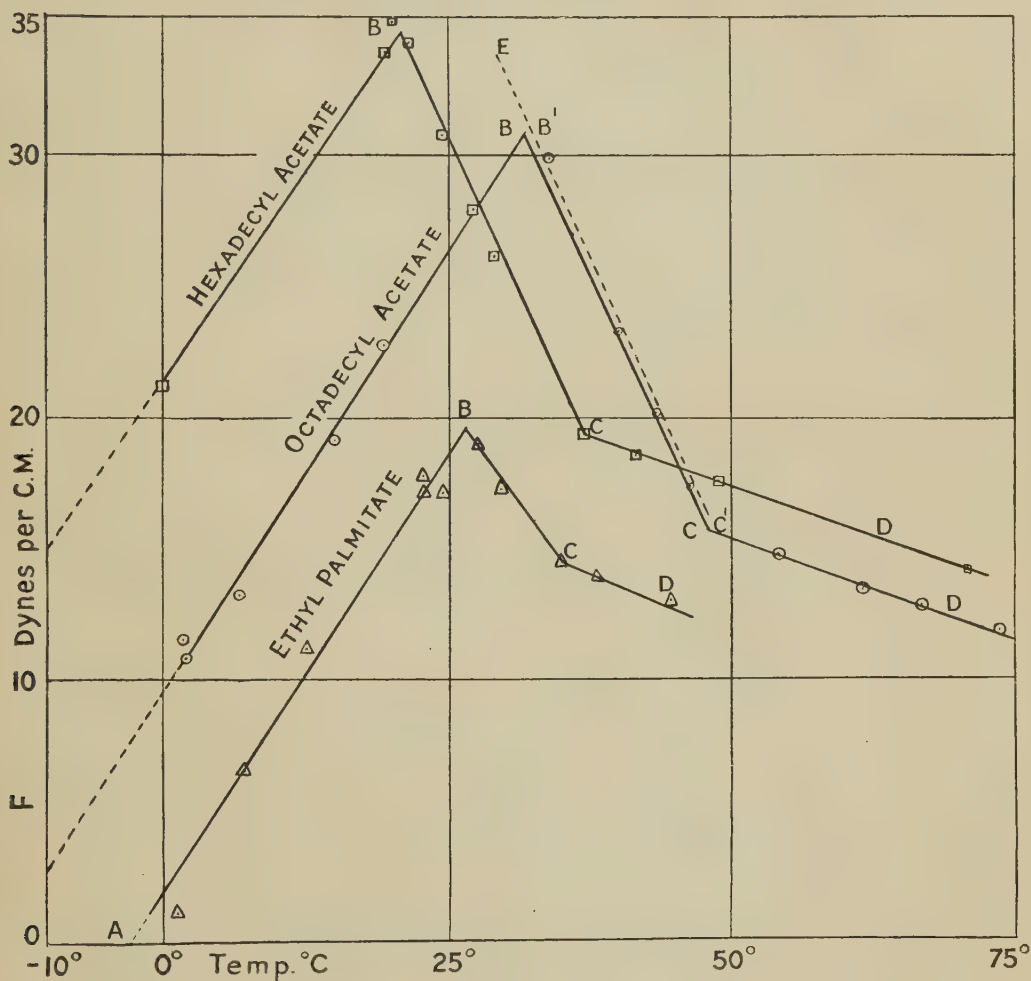


Fig. 2.

begins—the point A—cannot always be determined experimentally, as for some compounds it is far below the freezing point of N/100 HCl solution.

The dotted lines are prolonged to meet the temperature axis where feasible in this figure, but experimental points were not taken below the full lines.

The portion BC, in which the surface tension rises with the temperature, is

sensibly of the same slope for all three compounds, but differs slightly from the corresponding portion of the stearic acid curve. For the two acetates, differing only by two carbon atoms in the hydrocarbon chain, the length of BC is identical, and hence there is equality in both the temperature and in the F_e interval. For ethyl palmitate, BC is of the same slope, but is considerably shorter.

It may be pointed out here that neither bulk solubility, hydrolysis of the esters, nor volatility of the film can be determining factors in these equilibria. Bulk solubility can be of little influence, as the curves are very nearly exactly reversible, the dotted line in the case of octadecyl acetate representing experimental values obtained on cooling the surface from the point D. From C' to B' the path is practically identical with BC. Below B' the liquid is supercooled. Crystallization of the lens occurs at E, and the path then followed is again AB. Equilibrium is by no means instantaneous, requiring an increasingly longer time as the temperature is lowered.

Hydrolysis must be disregarded, as the same F_e is obtained 30 seconds after putting a crystal on the surface at a temperature above the melting point, as some hours later. Volatility of the film does not seem a possible factor, in that oleic acid has a constant slope from 10° C. to 70° C.

That at least one of these three possible effects is taking place to a limited extent seems to be indicated by the observation that the lenses float about with a slow but continuous motion at higher temperatures, although this may be due entirely to the increasing convection currents of air and water vapour to be expected immediately above the surface.

4. *General Discussion of Results.*

The behaviour exhibited by these systems can be interpreted on a basis of simple kinetic theory, while a thermodynamical consideration enables us to compare the energy relations concerned in two-dimensional changes of state with their more familiar prototypes in three dimensions.

It is of importance to notice that, while in the experiments of Langmuir and Adam the surface pressure or F value could be varied at will by altering the area available for each molecule in the surface, in the present case this pressure is entirely determined by the source of the film (crystal or lens), the surface concentration in the film at equilibrium attaining to a value which corresponds to and is defined by this equilibrium pressure. When this source is a crystal, evidence to this effect is found in an examination of the curve for myristic acid, fig. 1. At the points L.M. the F_e values are 7.9 and 15.5 dynes per cm. respectively. According to Adam's measurements, the film is therefore con-

densed at L (14.0°C.) and expanded at M (28.0°C.), and our own experiments on the rate of spread of these films (see Part I) are an additional proof that such is the case; yet the slope of AB is unaltered by these changes in the film proper, or, in other words, the slope is a function of the crystal. In the case of a liquid source, we have as the condition of equilibrium

$$\sigma_e = \sigma \cdot A + \sigma \cdot AB$$

or

$$\sigma \cdot \text{film} = \sigma \cdot \text{oil} + \sigma \cdot \text{oil-water}$$

or

$$F_e = \sigma_{\text{H}_2\text{O}} - (\sigma \cdot \text{oil} + \sigma \cdot \text{oil-water}) \quad (1)$$

for which it is again evident that the surface tension in the film, and hence the area per molecule, must adjust itself to satisfy the forces existing in the interfaces oil—water and oil—air. From this point of view, we may compare the film to a saturated solution in equilibrium with a solid, where the temperature may be raised and the solid undergo melting without any possible changes in the molecular condition of the solute itself, *e.g.*, association or dissociation, affecting the saturation pressure.

The behaviour of a typical compound is shown in the curve for octadecyl acetate, fig. 2. Along AB a crystal is in equilibrium with a film. This film may be condensed or expanded, or may change from condensed to expanded along AB without, as we have seen in the case of myristic acid, giving any evidence of the fact by a change of slope in AB. Neither is it possible, even with the most careful microscopic examination of the film during a gradual increase in temperature, to observe any *sharp* change from solid to liquid film. As Langmuir has shown, a liquid film may be solidified by simple compression; and since both the pressure and temperature are changing along AB a gradual conversion from solid to liquid film may be expected.

At B the crystal melts. Along BC and CD we have a *lens* in equilibrium with a film. From equation 1, $\sigma_{\text{oil}} + \sigma_{(\text{oil}, \text{H}_2\text{O})}$ must rise rapidly along BC and less rapidly along CD.

All pure liquids have a negative, and practically linear, temperature coefficient of surface tension. We must therefrom conclude that $\sigma_{\text{oil}, \text{H}_2\text{O}}$ is undergoing some change along B C, which is resulting in a high positive temperature coefficient; that this change is completed at C; and that C D represents a new type of interface, with a very much smaller positive coefficient.

Labrouste (4) and Adam (*loc. cit.*) have observed that all films can exist in two states of aggregation, which Adam denotes as condensed and expanded. In the former condition the area per molecule is small, and the temperature coefficient of expansion of such a film under constant compression is almost

negligible. At a well-defined temperature the condensed film begins to expand, occupying a greater area per molecule with increasing temperature, until after a range of the order of sixteen degrees has been traversed, the film is completely expanded, and further increase in temperature increases but slightly the area per molecule.

We may regard expansion in a unimolecular film as a gradual hydration and consequent separation of the polar heads, expansion being completed when the lateral attractions between the long hydrocarbon chains are sufficiently strong to prevent much further separation of the polar groups in the water. The suggestion is now made that true *interfaces* between oil and water or N/100 HCl may undergo the same process of expansion. Since the molecules in contact with water at such an interface undoubtedly possess the orientation characteristic of unimolecular films, there is every reason for supposing that at a definite temperature a similar hydration process would begin, going gradually to completion with increasing temperature; and that the effect during such a change would be to increase rapidly the interfacial tension oil—water. The “expanded” interface might then be expected to possess a low positive temperature coefficient of surface tension, corresponding with the low coefficient of expansion of expanded insoluble films as observed by Adam, and with the low temperature coefficients of the interfaces oil—water determined by Harkins (5).

With the experimental method used it is not possible to determine directly whether this expansion of the interface takes place simultaneously with that of the surrounding film. In any event, we may regard the expansion of the interface as taking place along B C, being completed at C. Along C D what may be referred to as a completely expanded interface is in equilibrium with what is, at this high temperature, undoubtedly an expanded film; but we have no direct means of knowing where the film began to expand, and indeed it may in some cases have been partly expanded at the melting point of the crystal.

Upon cooling the system under consideration from D, the path followed is sensibly that found with rising temperature, as far as the point B'. Supercooling of the lens may occur, in which case the path is B' E, as denoted by the dotted line in fig. 2. On the hypothesis of interfacial expansion taking place along B C, the portion B'E would indicate that the interface as first formed by melting of the crystal at B was already partly expanded. At E the lens crystallises, and if sufficient time is allowed for equilibrium, the path B A is followed with falling temperature. In the case of the shorter chain acids, which are somewhat more bulk soluble, the values obtained on cooling

a system from a high temperature are somewhat uncertain, and difficult to repeat; but for highly-insoluble compounds, the process seems to be entirely reversible, although some hours may be required for the attainment of the true equilibrium value.

In the case of octadecyl acetate the expansion interval with rising temperature is 16°C. , a value comparable with the expansion intervals observed by Adam when working under a constant compression of 1.4 dynes per cm.

If interfacial expansion is an analogous phenomenon, we might expect a similar progression with length of chain and melting point, in the temperature at which interfacial expansion commences, in any given series. Depending on the relation between this temperature and the melting-point, three possibilities are evident:—

(1) Melting occurs at a temperature such that the interface is completely expanded upon being formed, further increase in temperature elevating the interfacial tension but slightly, as the polar heads become slightly further separated by increased kinetic agitation. All the acids studied, with the exception of stearic, appear to belong to this category.

(2) Melting occurs at a temperature such that the interface as first formed is *partly* expanded. With increasing temperature the expansion would be completed, interfacial tension rising rapidly during the process. The three esters, as evidenced by the prolongation of C'B' to E on supercooling, and possibly stearic acid, may be regarded as examples of this class.

(3) The melting-point is at such a temperature that expansion of the interface has not yet begun. None of the substances investigated exhibit the behaviour to be expected of such a system.

5. Application of the Phase Rule and the Clapeyron Relation.

We may regard the film, whatever its state of aggregation, as one phase throughout the entire temperature range of the experiments, for the reasons already given. The compounds of the system are two: water and the organic compound. According to this view, the phases present at any time are as follows:—

The Esters and Stearic Acid:—

Phases along	{	A, B: solid in bulk, film, vapour.
		B, C: expanding liquid in bulk, film, vapour.
		C, D: expanded liquid in bulk, film, vapour.
Phases at	{	A: solid in bulk, water, vapour, film.
		B: solid in bulk; expanding liquid in bulk, film, vapour.
		C: expanding liquid in bulk; expanded liquid in bulk, film, vapour.

The other Acids :—

Phases along $\begin{cases} \text{A, B : solid in bulk, film, vapour.} \\ \text{B, D : expanded liquid in bulk, film, vapour.} \end{cases}$

Phases at $\begin{cases} \text{A : solid in bulk, water, film, vapour.} \\ \text{B : solid in bulk ; expanded liquid in bulk, film, vapour.} \end{cases}$

According to this view, the liquid water phase disappears as soon as the film has spread at the point A, from which we would conclude that the polar heads of the film are in chemical combination with the water of the underlying solution.

In justification of the assumption that water-vapour is present as a phase in these "two-dimensional" systems, it may be observed that the film is in reality of finite thickness, the polar heads being anchored to a number of water molecules. It has been shown by one of us (*Journal of Physical Chemistry*, 1925—in press) that water vapour passes through such films whether they are condensed or expanded, and is thus present between the hydrocarbon chains, while it is clear that in the extreme case of expanded films of the type of acetic acid, in which the lateral attraction between the hydrocarbon radicles is negligible, water-vapour plays a considerable part in the mechanism of dynamic equilibrium.

The Clapeyron relation as ordinarily stated

$$\frac{dP}{dT} = \frac{\lambda}{T(V_2 - V_1)}$$

may be applied in the present case in the form

$$\frac{dF}{dT} = \frac{\lambda}{T(A_2 - A_1)},$$

in which A_2 is the area occupied by a gram molecule of the compound in question in the form of a film (condensed or expanded) and A_1 the area occupied by a gram molecule in bulk (solid or liquid).

If we knew the area per molecule at the point B, the calculations made by using the algebraic sum of the slopes of AB and BC as dF/dT would give the latent heat of fusion of the crystal in question.

The present experiments afford no means of determining the exact area at the melting period. In the case of stearic acid and of the three esters we have given reasons for believing the film is largely condensed. The areas used in the calculation are those of the polar heads "under zero compression." These are probably a few per cent. higher than the areas actually occupied

by the films at the melting point of the crystal, but the *relative* areas of the different polar heads are most accurately expressed by these numbers.

Table I.

Compounds.	Number of C atoms in chain.	$\frac{dF}{dT}$ in dynes/cm.° C. along.				Abs. Temp. at			FeAT B.	λ Calculated.	Assumed area per Mol. at B in Å.U.
		AB.	BC.	CD.	BD.	A.	B.	C.			
Decylic acid	11	0.588	—	—	-0.153	233.0	298.0	—	38.2	—	—
Undecylic acid	12	0.548	—	—	-0.153	254.0	318.0	—	35.1	—	—
Dodecyl acid	14	0.568	—	—	-0.153	273.0	327.0	—	30.7	—	—
Tridecyl acid	15	0.552	—	—	-0.153	266.0	325.0	—	32.6	—	—
Myristic acid	16	0.554	—	—	-0.153	278.0	336.0	—	32.1	—	—
Stearic acid	18	0.553	-0.670	-0.153	—	290.0	344.0	350.0	29.9	15.200	25.0
Myristic acid	17	0.517	—	—	-0.071	221.0	280.0	—	30.5	—	—
Octadecyl acetate	16	0.637	-0.940	-0.153	—	240.0	294.0	310.0	34.4	15.400	23.0
Octadecyl acetate	18	0.667	-0.930	-0.153	—	259.0	305.0	321.0	30.7	16.200	23.0
Octadecyl palmitate....	16	0.669	-0.853	-0.153	—	271.0	300.0	306.0	19.4	14.500	22.0

The value of λ for stearic acid as given in Beilstein is unquestionably low, namely, 13,500 calories. An extrapolation, using the latent heats given by Gärner and Randall (6) and Stratton and Partington (7), gives the figure 15,000 calories. Our calculated value is 15,200 calories. The latent heats of the esters have not been determined calorimetrically. The calculated values are of the order to be expected.

The latent heat of spreading of solid stearic acid, as calculated at the point A from the slope of AB and assuming an area of 25 Å.U., is 5,780 calories per gram molecule.

The amount of pure compounds at our disposal was insufficient to allow of further verification of the hypothesis of interfacial expansion by measurements of the temperature coefficient of surface tension of the interface oil-water with the drop-weight method. The capillary-rise method is unsatisfactory for such measurements, since the movement of the meniscus introduces the question as to whether the glass walls of the capillary are wet by the oil or the aqueous solution. Qualitative experiments with this method on octadecyl acetate, however, showed that the quantity

$$\sigma_{\text{oil}} + \sigma_{\text{oil, H}_2\text{O}}$$

risks rapidly from the melting point to about 47.0°C ., beyond which temperature there is only a slight increase in the sum of the two surface tensions.

Oleic acid, on the other hand, showed no such break, $\sigma_{\text{oil}} + \sigma_{\text{oil.H}_2\text{O}}$ increasing very slightly with rising temperature, as we should expect from the absence of any portion BC, and the slope of BD, fig. 1.

Garner and Randall (*loc. cit.*) have shown that the fatty acids with an odd number of carbon atoms can exist in two forms, α and β , which are characterised by well-defined transition temperatures. We should accordingly have anticipated a break in the curve for this acid at the transition temperature. Very careful experiments with this compound, as well as with pentadecylic acid, failed to reveal any alteration in slope of AB. For the present we can advance no plausible explanation, although there is a possibility of immediate racemisation of the unstable form of the carboxyl group (when brought into contact with water) to which, according to Garner and Randall, the allotropic modification owes its existence.

Summary.

1. The effect of temperature on the pressure of a film in equilibrium with a crystal or lens of various organic compounds, containing a long chain and terminating in a polar group, is considered in detail for the fatty acids and their esters. The stability of unimolecular films of fatty substances on water is directly related to this equilibrium pressure.

2. With some compounds the water—oil interfacial tension is shown to rise rapidly with increasing temperature. An explanation is advanced, in which it is suggested that such an interface can exist in either of two modifications corresponding to the condensed and expanded states of unimolecular films.

3. The phenomena are discussed from the standpoint of the phase rule. By an application of the Clapeyron equation the latent heat of fusion is calculated for some of the organic compounds studied.

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The Behaviour of Crystals and Lenses of Fats on the Surface of Water—Part III. The Effect of the Polar Group on the Equilibrium Pressure.

By ARTHUR CARY and ERIC KEIGHTLEY RIDEAL.

(Communicated by Sir William Hardy, Sec. R.S.—Received June 17, 1925.)

The method of determining surface tension was that of measuring the force required to pull a platinum ring through the surface, as described in previous papers (1) (2). N/100 HCl solution was employed throughout. The organic compounds used were of such purity that the tension at equilibrium was, with certain exceptions to be noted later, independent of the amount of fat placed on the surface.

At high temperatures some of the compounds studied, particularly the palmitates, were somewhat soluble. In these cases care is required to ensure that there is an excess of the ester present as a crystal or lens. This solubility did not, however, affect the equilibrium tension, the same values being obtained shortly after inoculating the surface and some hours later.

The "impure" oleic and lauric acids with which the results in fig. 2 were obtained were B.D.H. preparations used without further purification. The other compounds were from the collection of N. K. Adam, the same preparations as were used in his determinations (3).

1. *The Palmitates.*

Fig. 1 gives the variation of the equilibrium surface tension with temperature for surfaces of N/100 HCl, saturated with the normal esters methyl, ethyl, and propyl palmitates. According to the hypothesis of "interfacial expansion," advanced in Part II to account for the rapid rise in surface tension (corresponding to a fall in the value of F_e), observed along BC (B being the melting point), the interfaces oil—water of these compounds are partly condensed at the melting point, expansion taking place along BC, being completed at C. The values were reversible to the extent described in Part II for the acetates. Supercooling was possible in all three cases, the line CB being prolonged beyond B without change in slope with falling temperature. When crystallization occurred, the path followed was then BA, but some time was generally required for the attainment of equilibrium.

As pointed out in Part II, the condition of the film, *i.e.*, whether condensed

or expanded, has no influence on the shape of the curves ; but, by a comparison with Adam's (*loc. cit.*) curves, it is possible to evaluate with reasonable accuracy

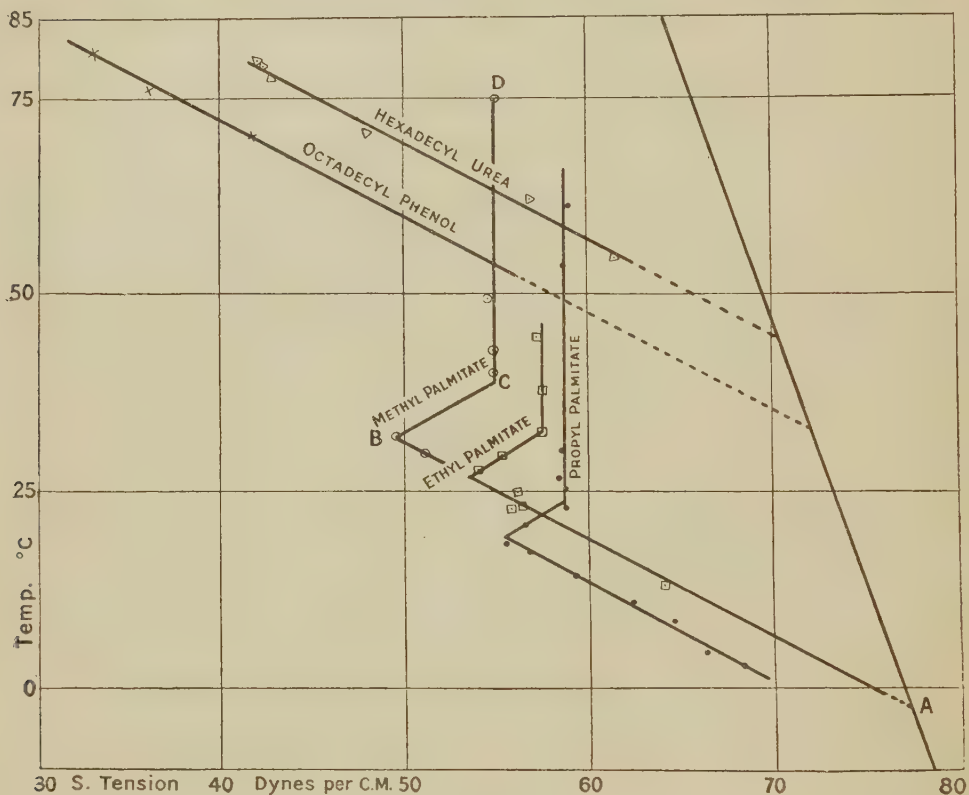


FIG. 1.

the area occupied per molecule of the *film* at any given point. Such a comparison leads to the conclusion that the films of all three esters are in the condensed state at the melting point, and the areas used in calculating the latent heats of fusion have been evaluated accordingly.

Table I gives the collected data. The latent heats of fusion, as calculated from the difference of the slopes of AB and BC, employing the Clapeyron relation as before, give values of the proper order, but as no calorimetric determinations have been made on these compounds, it is impossible to estimate more closely the probable error of this type of calculation.

Table I.

Compound.	Absolute temperature at			dF/dT in dynes per cm. °C. along			Assumed area per molecule in Å.U. at B.	F ϵ .	λ calculated.
	A.	B.	C.	AB.	BC.	CD.			
Methyl palmitate	271	305	312	0.669	-0.952	-0.153	22	22.9	15,700
Ethyl „	271	300	306	0.669	-0.853	-0.153	22	19.4	14,500
Propyl „	263	292	297	0.635	-0.850	-0.153	22	18.5	13,800
Octadecyl methyl-ether	263	304	323	0.537	-0.769	-0.109	20	21.9	11,500
Palmito nitrile	232	305	310	0.888	-0.362	-0.139	28	21.0	15,400
Hexadecyl urea	318	—	—	0.656	—	—	—	—	—
Octadecyl phenol	306	—	—	0.656	—	—	—	—	—

2. Other Compounds.

Fig. 1 also gives the experimental values obtained with hexadecyl urea and octadecyl phenol. The temperature at A is surprisingly high. In both cases

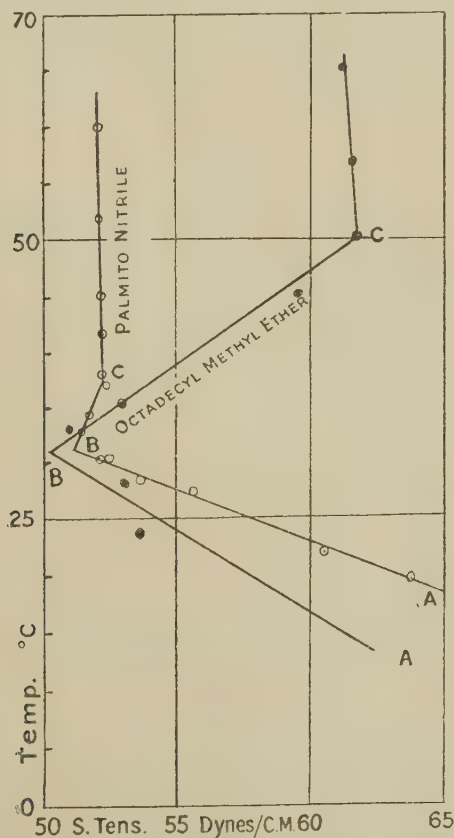


FIG. 2.

the system was allowed to remain for some hours at a temperature a few degrees below the A temperature ; but no fall in surface tension was observed. The melting points were not reached experimentally.

In fig. 2 are shown the values for octadecyl-methyl ether and palmito nitrile. The points for the first-named compound were difficult to repeat along AB, *i.e.*, before melting of the crystal occurred at B, from which it seems likely that there was some impurity present. There is, however, the possibility that the film is not as stable as those formed with compounds possessing more strongly polar heads, as indicated with Adam's results with the same ether, in which case the equilibrium at the surface might be disturbed by pulling the ring through the surface. In calculating the latent heat of fusion for this compound, we have assumed an area per molecule corresponding to a condensed film, *viz.*, 20 Å.U., but as Adam gives no temperature of half expansion, it is not possible to say how far this assumed area is correct.

It is interesting to observe that the portion BC of palmito nitrile has a comparatively low negative value for dF/dT , while the slope of AB is the highest of any of the compounds studied. Nevertheless, the latent heat as calculated is of the proper order, since the area of this polar head is somewhat large.

3. *The Linear Nature of the Curves.*

That the behaviour of all the systems thus far studied can be represented by a series of straight lines, the various portions in any given series being sensibly parallel, is reminiscent of the results obtained by Hardy (4) in his investigation of the lubricating properties of similar series of long-chain compounds. The interpretation would appear to present considerable difficulty. In general, the lower the melting point of a given compound in any series, the lower the "A" temperature, and the higher the F_e value at any temperature. But an exception is found in methyl and ethyl palmitates, the melting points of which differ by 5° C., while the "A" temperatures are the same. Further, an examination of Table I shows that when the terminal polar group of a C 16 chain is changed from COOH in palmitic acid (Part II) to the various more or less complicated heads, such as the methyl group, &c., the "A" temperature may change by an amount equal to, greater than, or less than, the corresponding change in the melting point of the crystal.

In this respect the only general conclusion which seems to be suggested by the data at present available is to the effect that the slopes along AB and CD are determined by the hydrocarbon chain, while the slope of BC depends

on the polar group. It is hoped that further experiments on other series may lead to a better understanding of these relations.

4. Impure Compounds and Mixtures.

In fig. 3 are shown the results obtained with commercial oleic and lauric acids. (See Part II for the values for these acids after purification.) The

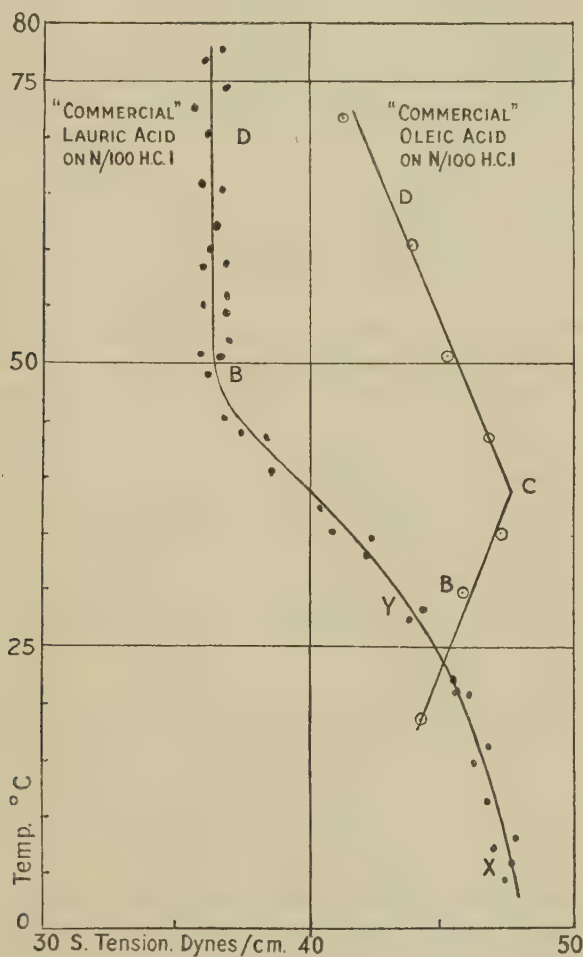


FIG. 3.

equilibrium values for this oleic acid appeared independent of the quantity with which the surface was inoculated. Lauric acid, however, seemed to possess some impurity, probably a lower fatty acid, which was cumulative in effect.

While pure oleic acid shows no portion BC, the present compound gives a sharp change in slope at C, a possible explanation for which will be discussed later. Experimental values were not obtained below the melting point, and the portion AB is accordingly lacking.

The curve for lauric acid is of interest chiefly in that it is typical of the behaviour of all but the most highly purified compounds. All so-called "pure" preparations as supplied by the chemical houses, even though characterized by a fairly sharp melting point, give a similar type of curve. The lower portion, XY, is obviously determined by the CD portion of some impurity present. Along YB the effect is that corresponding to the AB portion for pure compounds; and after the melting point at B, the behaviour is approximately that of a pure compound.

These observations made it of interest to determine the effect of mixing two pure compounds, that is, of inoculating the surface with two different compounds in the same experiment. The first combination tried was that of stearic acid dissolved in liquid oleic acid (pure). The observed values were exactly the same as those obtained with oleic acid alone. Pure paraffin oil (B.D.H. "internol") mixed with oleic in varying proportions also gave the same results as pure oleic acid alone.

For hexadecyl and octadecyl acetates the results are as shown in fig. 4. The full lines represent the acetates as determined separately, the dotted line is for the combination. The same curve was obtained regardless of which compound was first placed on the surface, nor did the addition of further amounts of either component during the experiment alter the slopes of the different portions in any way.

It is seen that the tension is determined by the component capable of lowering the surface tension to the greater extent, as far as B', the melting point of the octadecyl acetate. Instead of following B'D', the curve continues without change in slope to a point B'', beyond which B''C'' and C''D'' are sensibly parallel to the corresponding portions of the separate acetates.

The effect is somewhat surprising, this being the first example of the general slope AB being prolonged beyond the melting point. In particular, it seems significant that the absolute amount of either component present is not an influencing factor. Further experiments are required to ascertain if this result is general. However, it may be tentatively suggested that during the process of evaporation and condensation taking place around the edges of the lenses, a thin annular ring of constant composition might be established, characterized by a definite solution pressure higher than that of either component,

and with properties comparable to those of a solid solution. The composition of this ring would depend only on the composition of the film, which would in

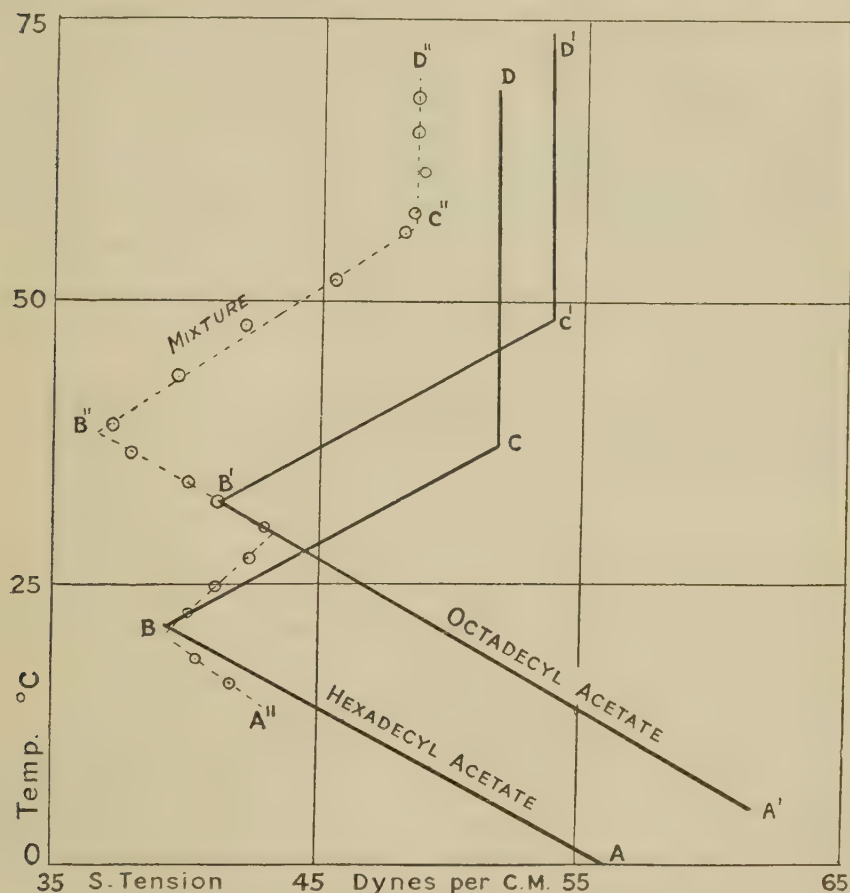


FIG. 4.

turn be independent of the absolute amounts of either component present. The temperature coefficient of surface solubility of the outside ring might then be the same as that of a crystal, the observed tension in the film falling with rising temperature, until interfacial expansion began at B'', resulting in a change in slope from that of AB to that of the direction of BC. We have observed with experiments on mixtures that the lenses at times appeared distorted from the normal perfectly circular shape.

Whatever the true explanation, it seems probable that the appearance of a portion, BC, in commercial oleic acid is due to an impurity exerting a similar effect.

Summary.

1. The study of the effect of temperature on the equilibrium surface tension resulting from the spread of a film from a crystal or lens of an organic compound on a surface of N/100 HCl, begun in Part II, is continued for a number of long-chain compounds with more complicated polar heads.

2. The latent heats of fusion are calculated from the Clapeyron equation.

3. The effect of impurities, and of inoculating the surface with two different compounds, is considered; but further experimental evidence is required for a full understanding of the somewhat involved systems thus obtained.

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On the Stress-Optical Effect in Permanently Overstrained Celluloid.

By S. R. SAVUR, University College, London.

(Communicated by Prof. L. N. G. Filon, F.R.S.—Received June 16, 1925.)

1. In a recent paper Dr. M. Wächtler (1), repeating and extending some previous experiments of H. Ambronn (2), has found that the residual double refraction in permanently overstrained celluloid, instead of increasing with the permanent strain, reaches a maximum and begins to decrease. For a permanent strain varying between 11 to 18 per cent. extension of the specimen (according to the wave-length of the light used), Wächtler states that the residual double refraction vanishes, and for higher values of the permanent strain he finds it to become negative and to increase negatively until the rupture limit is reached. This same phenomenon of reversal of double refraction had been previously observed by Ambronn (7). Wächtler bases upon this result certain severe criticisms upon the use of celluloid models for exploring the stresses in engineering structures, a method which has been employed of late years, with conspicuous success, by Prof. E. G. Coker (3).

Wächtler, in the paper referred to, comments on the fact that neither Coker

and Chakko (4), nor Filon and Jessop (5), in their investigations upon the law of artificial double refraction in celluloid, refer to the results of Ambronn, which were published in 1911.

It may be at once mentioned that, even admitting the correctness of Ambronn's and Wächtler's results for permanent extensions ranging from 3 or 4 to 50 per cent., neither Coker and Chakko, nor Filon and Jessop, have used strains approaching at all to such values; in the case of the last two investigators the results show that the specimens eventually exhibited complete recovery, so that *permanent* strain did not come in question. And since, in engineering investigations on celluloid models, the stresses are usually much below the values employed by Filon and Jessop, the criticisms of Wächtler, as to the validity of the results of such stress explorations, hardly appear legitimate.

From the point of view of Pure Physics, however, the results of Ambronn and Wächtler appeared so remarkable as to justify an independent verification, and the experiments described below were undertaken with this point in view.

2. The material employed throughout in this investigation was the form of celluloid known as xylonite, and was supplied by the British Xylonite Company. It is (at least nominally) identical with the material generally used by Prof. Coker in his investigations, and by Filon and Jessop in the research already cited. In fact, some of the specimens used by Filon and Jessop were actually employed.

The specimens were cut from a plate about 7 mm. thick and their shape and dimensions were as shown in fig. 1, the cross-section in the middle part being approximately square. The straining frame and the optical arrangements were similar to those used by Filon and Jessop and described by them, the relative retardation being measured by means of a Babinet compensator. It was not necessary, however, to use a lever extensometer to observe the elongation and lateral contraction, both of which were considerable; and these were directly observed by a simple micrometer. The centering of the knife-edges, which carried the load, could be made with such accuracy that, even under the maximum load used, which

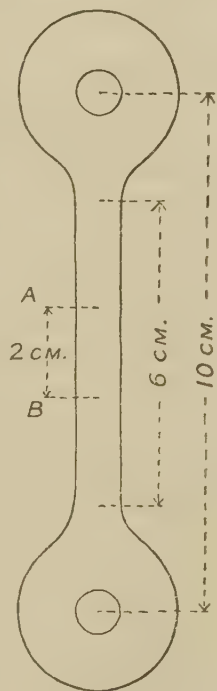


FIG. 1.

gave a relative retardation of $9\frac{1}{2}$ wave-lengths for sodium light, the band in the Babinet compensator remained sensibly horizontal over a length AB of the specimen extending to 1 cm. on either side of the middle cross-section.

3. A tension of about 300 bars being now applied to the specimen, the total relative retardation, observed immediately after loading, was approximately 5λ for sodium light. "Creeping" then set in vigorously, the retardation being $9\frac{1}{2}\lambda$ after half-an-hour. After this there was little change, though the load was kept on for three days. The load was then completely removed and the specimen kept under continuous observation; the retardation was observed to diminish steadily, the passage of the bands, as they recrossed the datum line, being carefully noted. In the course of about 10 hours the retardation had diminished to $5\frac{1}{2}\lambda$ and after a further 24 hours to 5λ , at which value it still remains 3 months after unloading.

The corresponding maximum stretch was simultaneously observed to be 36 per cent. and the residual stretch eventually was 34 per cent., a value which has likewise been permanent.

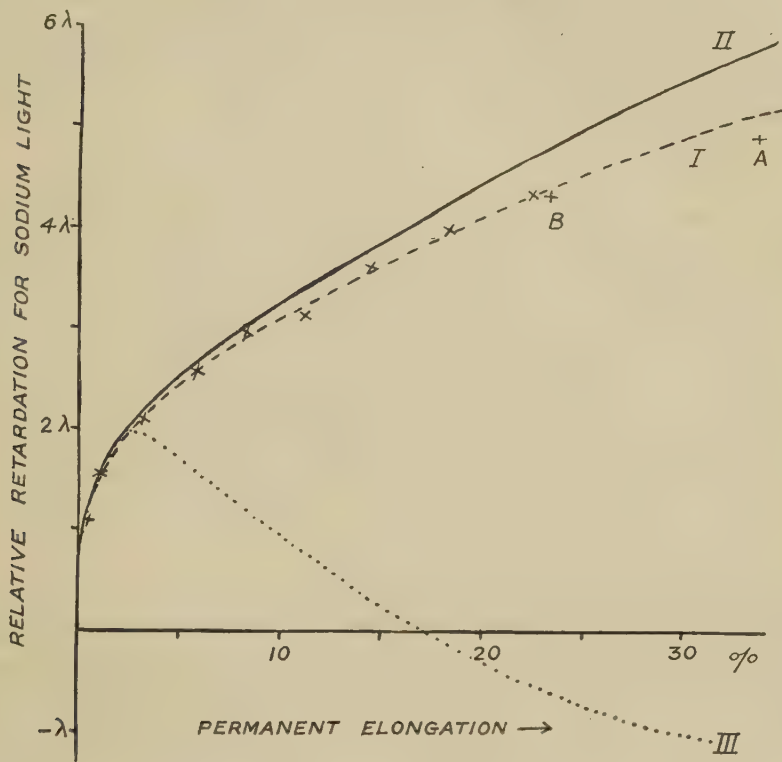
Other loads were also tried, with similar effects. It was found however, that, if the stress exceeded 400 bars, a very rapid creep set in which quickly led to fracture, the yield point of the material having been reached.

Fig. 2, curves I and II, show the residual relative retardations for various permanent elongations of another specimen up to 30 per cent., this being the maximum elongation which the specimen was found to stand without rupture when given successive increments of permanent stretch. The curve I shows the actual residual relative retardations observed, the curve II the retardations corrected for the change of thickness due to lateral contraction and reduced to the "unstrained thickness."

As will be seen, there is *no tendency to reversal*: the residual relative retardation per unit thickness (*i.e.*, the difference $n_e - n_o$ between the extraordinary and the ordinary indices of refraction) increases steadily with the permanent elongation, although, of course, it is not proportional to it. But there is no trace (up to breaking point) of a maximum, still less of vanishing or reversal of double refraction.

4. This result being in complete contradiction with that announced by Ambronn and Wächtler, it appeared desirable to verify the values of the residual retardations by an independent check, in case any miscount of the bands should have occurred, or an undetected recovery should have taken place during the night, when, of course, the specimen could not be observed, however unlikely such an occurrence might appear.

A direct determination of the order of the band with the Babinet proved extremely difficult. In the case of homogeneous light no means existed for



A, B are points obtained from two other specimens given their permanent extensions at one stretch.

FIG. 2.

determining the zero. In the case of white light, however, owing to the (unknown) difference of the dispersion of double refraction in the quartz of the Babinet and in the celluloid specimen, it was felt that any attempt at fixing the order of the band by observing the position of the *black* band in the Babinet would be attended by so much uncertainty as to be worthless.

In order to get over this difficulty the Babinet was replaced by a horizontal celluloid strip CD (fig. 3) bent as shown (but much exaggerated in the diagram). Owing to the stress-gradient from top to bottom of the strip, it became, in effect, equivalent to a Babinet, and it was confidently expected that, owing to the dispersion of double refraction being identical in the celluloid and in the strip (both of which were cut from the same plate), the black band in the part where

the strip and the specimen *S* overlapped would indicate accurately, when produced into the non-overlapping parts (see fig. 3), both the sign and the order of the residual double refraction; and undoubtedly, if the *neutral* bands could have been identified in the two cases, the vertical distance between them, measured in terms of the distance between consecutive bands, would have indicated the relative retardation.

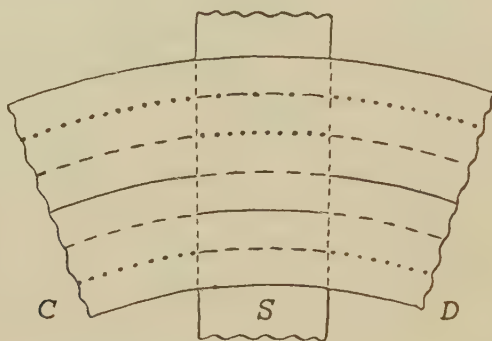


FIG. 3.

5. When this experiment was actually carried out with the specimen above-mentioned, the appearance of the bands was as shown in fig. 3. The black bands are there shown by full lines, the coloured bands by interrupted or dotted lines. The position of the black band, however, instead of indicating a *positive* retardation of 5λ , showed a *negative* retardation of 1λ , to all appearance verifying Ambrohn's result and contradicting the conclusion derived from continuous observation of the history of the specimen.

6. This immediately threw considerable doubt upon the whole matter. At the suggestion of Prof. L. N. G. Filon, the following independent method of estimating the sign and amount of the double refraction was then tried.

The Babinet was once more put in position (the white light being replaced by sodium light) and the specimen was then rotated about a vertical axis (*i.e.*, one parallel to the line of strain) through an angle θ which could be measured.

Since the wave surface in the specimen is, in this case, necessarily of the uniaxial type with the optic axis parallel to the line of strain, the only difference introduced by this rotation is the additional length of path in the specimen. This is readily computed, from the ordinary laws of refraction through a plate, to be

$$c \left(\sqrt{n^2 - \sin^2 \theta} - 1 \right), \quad (1)$$

where c is the thickness of the specimen and n is the ordinary index of refraction of the strained specimen.

If then Δr is the change in retardation, due to this rotation, this change of retardation can be easily followed and measured in the Babinet, and if r be the whole retardation

$$\frac{\Delta r}{r} = \frac{n}{\sqrt{(n^2 - \sin^2 \theta)}} - 1, \quad (2)$$

whence r is known, both in sign and magnitude.

It was found sufficient to measure θ to about 1° and n to about 1 per cent. This leads to a determination of r correct to approximately 5 per cent. But the fractional part of r is determined from the Babinet with great accuracy, the only difficulty being here to determine the integral number of wave-lengths.

n was determined by an independent experiment as 1.31. θ being 30° , Δr was found to be $+0.42\lambda$, which immediately showed that the residual double refraction was indeed *positive*, as originally determined. Substituting in equation (2), it is found that

$$r = 5.2\lambda, \text{ approximately.}$$

Now the Babinet reading (for normal incidence) was $(x + 0.99)\lambda$. It follows at once that $x = 4$ and that the correct value of r is 4.99λ , thus confirming the earlier calculation.

7. The inevitable conclusion is then, that, in the experiment described in paras. 4 and 5, the black band observed in the overlapping part was *achromatic* without being *neutral* (*i.e.*, corresponding to *zero* retardation). As this could not possibly be the case if the law of dispersion of double-refraction were the same in the specimen and in the comparison strip under flexure, this leads us to inquire what the effect should be, if this assumption be not made.

Let Δn be the difference of the ordinary and extraordinary refractive indices for wave-length λ in the overstrained specimen, *i.e.*, the residual double refraction, reckoned positive if in the same sense as would be produced by a tension in unstrained celluloid.

Let C be the stress-optical coefficient of the comparison strip for such (moderate) stresses as were used.

Then the total relative retardation at distance y above the neutral axis of the bent strip (fig. 3) is $c \cdot \Delta n - (C \cdot My/I) c$ for the light of wave-length λ , where M is the bending moment and I the second moment of the cross-section about the neutral axis; c is the thickness of either piece.

Light of wave-length λ is extinguished at that point if

$$c \cdot \Delta n - \frac{C \cdot My}{I} c = p\lambda,$$

p being an integer and the true order of the resultant band.

Now, if the band seen is sensibly achromatic, the value of y must be independent of λ , at any rate to the first order; hence

$$\frac{d}{d\lambda} \left(\frac{\Delta n}{\lambda} - \frac{C}{\lambda} \cdot \frac{My}{I} \right) = 0$$

or

$$\frac{d}{d\lambda} \left(\frac{\Delta n}{\lambda} \right) = \frac{My}{I} \frac{d}{d\lambda} \left(\frac{C}{\lambda} \right).$$

It follows that, if such a band be observed, as was the case in fig. 3, *below* the neutral axis (y negative), then $d/d\lambda (\Delta n/\lambda)$ and $d/d\lambda (C/\lambda)$ must have *opposite* signs.

8. This conclusion may be readily tested by means of the spectrum method described by Filon (6). Light is passed through two crossed nicols and a specimen under uniform stress is analysed in a spectroscope, and the spectrum is seen to be crossed by black bands corresponding to the values of λ given by

$$p\lambda = CTc,$$

where T is the tension, in the case of a specimen under stress (and without residual retardation), or by

$$p\lambda = c \cdot \Delta n$$

in the case of a specimen with residual double refraction Δn . If now the specimen is rotated about the axis of stress (or optic axis), as explained in para. 6, c is effectively *increased* by a quantity given by equation (1). Calling this δc and remembering that it is essentially positive, we see that, if $\Delta n/\lambda$ or C/λ *decreases* with λ , the band of the p th order will move in the direction of increasing λ , *i.e.*, towards the red, on the specimen being rotated from the position of normal incidence in either sense. The same effect will be produced, in the case of a specimen under tension, by increasing the stress.

Now the above is what is observed in the case of every ordinary material. And, in fact, an unstrained piece of celluloid being subjected to this test under gradually increasing tension, the bands of the successive orders up to the eighth were observed to come in at the violet end and to move towards the red, and also, on the specimen being rotated, the bands moved towards the red in every case.

But it was noticed that this shift towards the red on rotation became *less marked* as the stress was increased. Also that the bands of later orders moved more slowly red-wards than would have been expected; and further that the bands did not, as is normally the case in this experiment, become sensibly sharper as the order of the band increased. All these observations point clearly, to the same conclusion, that, as the loading progresses $d/d\lambda (C/\lambda)$, while still remaining negative, diminishes numerically as the load is increased.

When, however, the specimen, which had been strained until it showed a retardation of $9\frac{1}{2}\lambda$ and then allowed to recover so that it had a residual retardation of 5λ , was subjected to the same test, and rotated, the band was observed to shift *definitely towards the violet*, showing that for this overstrained specimen $d/d\lambda (\Delta n/\lambda)$ was now positive.

9. It appears, therefore, that what does happen in celluloid, if subjected to progressively increasing tension, is that its law of dispersion of double refraction becomes progressively modified in such a way as to approach achromatism (this last will occur when $d/d\lambda (C/\lambda) = 0$, or, in the case of a permanently doubly-refracting specimen, when $d/d\lambda (\Delta n/\lambda) = 0$). That the stress-optical coefficient itself increases with the wave-length for the higher loads is clear; and, indeed, this increase in the stress-optical coefficient with the wave-length is not unique, for certain glasses have been found to show the same effect. But what appears to be quite unique is the fact that, at any rate in specimens in which a large permanent double refraction has been introduced by overstrain, the dispersion is such that the double refraction increases towards the red *more rapidly even than the wave-length itself*, thus reversing the standard order of colours. Such an anomalous dispersion of artificial double refraction does not appear to have been observed hitherto.

10. The conclusion arrived at in the last paragraph was confirmed and made more definite by the following observation. A strip of celluloid was placed normally to the rays and examined by the spectrum method whilst subjected to progressively increasing stretch in a straining frame. The bands moved across the spectrum in the usual manner, exhibiting, however, the peculiar characteristics described in paragraph 9 when a fairly high order of band was reached. On rotation, the bands invariably moved towards the red, showing that the normal order of colours still held good.

On unloading, however, the specimen (which was found by the method of paragraph 6 to have a permanent residual retardation of $3\cdot8\lambda$ in sodium light), and examining it by the spectrum method, a band was visible in the indigo, and there was a visible shortening of the red end of the spectrum, which showed

the existence of another band partly in the red and partly in the infra-red. When the specimen was rotated about its optic axis, the band in the indigo moved towards the violet, showing that $d/d\lambda (\Delta n/\lambda)$ was now *positive* for that wave-length. The red end of the spectrum, however, lengthened and brightened showing that the band here had moved towards the infra-red so that $d/d\lambda (\Delta n/\lambda)$ was still *negative* for red light.

It follows that $\Delta n/\lambda$ must be a maximum for some intermediate wave-length, a fact which could be made visible by the following method, which also provided a means of approximately determining the wave-length for which the maximum occurred.

A gradually increasing (but moderate) tension was applied to the specimen. After a short time the whole field from the red to the blue became altogether dark. On increasing the tension, light was then restored in the yellow, giving the appearance of a broad bright band on a dark field; on further increasing the stress, two dark bands were now observed to move outwards, one towards the violet and one towards the red. On increasing the tension still further the field became altogether bright and then *suddenly* darkened all over, this being followed by the re-appearance of yellow light and the opening out of two black bands as before.

The explanation of these remarkable appearances will be obvious from the diagram (fig. 4). For if Δn be the residual double refraction and C the stress-

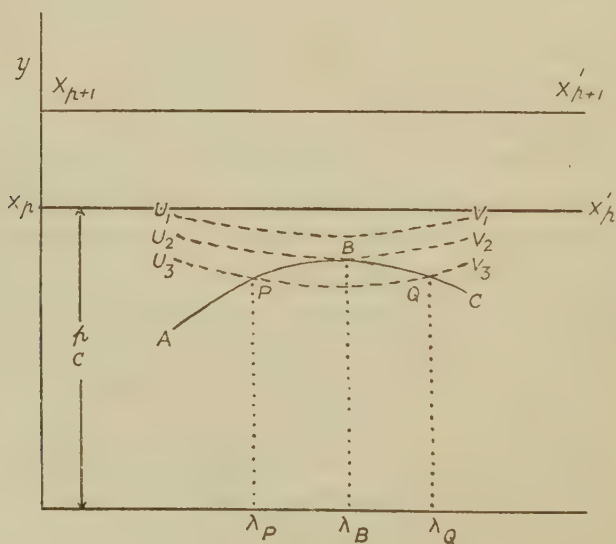


FIG. 4.

optical coefficient in the specimen, the equation determining the position of the band of p th order is $p/c = \Delta n/\lambda + CT/\lambda$, where T is the additional tension applied and c the thickness of the specimen.

Let the curve ABC (fig. 4) give the graph $y = \Delta n/\lambda$ plotted to λ , the curve having a maximum in the visible spectrum. Let the straight line $X_p X'_p$ represent the line $y = p/c$, and let the curve UV be obtained by subtracting from the ordinates $X_p X'_p$ the amount $(C/\lambda)T$, so that the vertical distance between UV and $X_p X'_p$ measures, on scale proportional to the additional tension, the quantity C/λ .

At first, when T is zero, since $X_p X'_p$ does not cut the curve ABC, no band of order p exists in the field. For a small tension T_1 , UV has the position $U_1 V_1$ and still does not intersect ABC, and the field remains bright. If, however, T is increased to a value T_2 such that UV reaches a position $U_2 V_2$ in which it touches ABC at B, a single band will appear for the wave-length λ_B . This band, owing to the close approach of the two curves over a considerable area, is of a large extent, a great portion of the spectrum being dimmed. If now T be increased to T_3 , the curve UV is lowered to the position $U_3 V_3$, in which it intersects ABC at two points P, Q on either side of B. We then have light restored for λ_B and two bands on either side, at λ_P and λ_Q , which move outwards. As the stress is increased, a similar effect will occur for the band of $p + 1$ th order, and so on.

The actual law of variation of C with the wave-length has not yet been determined for the overstretched specimen. If, however, we assume that the law of dispersion is the same for the residual and the added double refraction, so that

$$C = k \cdot \Delta n,$$

where k is independent of λ , the equation for the p th order band becomes

$$\Delta n/\lambda = p/c (1 + kT),$$

and the intersections are then defined by the curve ABC and a horizontal straight line [$y = p/c (1 + kT)$], which is lowered as k increases. The point B, where the darkening and subsequent brightening occur, will then be the point where ABC has a horizontal tangent—that is, the point where $\Delta n/\lambda$ is a maximum.

By applying this method to a number of specimens of varying permanent elongation, it was found that the position of this maximum in the spectrum

varied, the wave-length λ_B increasing with the permanent stretch as follows:—

Permanent Stretch. (Per cent.)	Region of Spectrum where maximum occurs.	
14	Green,	about 5400 Å.U.
17	Yellow-green,	„ 5700 Å.U.
26	Orange,	„ 6000 Å.U.

No accurate determination of λ_B was attempted, in view of the uncertainty introduced by our present ignorance of the law of dispersion in *C* when additional load is reimposed upon the overstretched xylonite. Experiments are, however, in progress to determine this law quantitatively by a modification of Filon's spectrum method (6).

11. The question arises whether this effect may not account for the discrepancy between the results of the present investigation and those previously found by Ambronn and Wächtler.

Ambronn [(2), p. 251] appears to have determined the residual double refraction of his permanently over-stretched celluloid strip by matching the colours shown by it in white light between crossed nicols with those exhibited by a quartz wedge in white light between crossed nicols. This seems to be identical in principle with the method shown in fig. 3, where the common black band is to be assumed to be the true zero band. Though Wächtler does not give the method by which he determined the residual double refraction of his permanently overstrained celluloid strips, it is very probable that his was similar to Ambronn's. We shall now see what results we are led to by this method in our case.

Returning to the experiment of paras. 4 and 5, the *apparent* residual double refraction in the specimens was calculated on the assumption that the *achromatic* band was a true *neutral* band. This was done for various permanent elongations and the results are shown in curve III, fig. 2. Up to (true) residual retardation 2λ , the band observed remains the true neutral band and curve III remains identical with II. But, when the true residual retardation is 3λ , there is, strictly speaking, no black band to be seen; the band one above the neutral band in the margins is the least coloured. This gives an apparent residual retardation 1λ . When the true residual retardation is 4λ , this least coloured band, which now approximates to blackness, coincides with the neutral band in the margins. The apparent residual retardation is, therefore, zero. When the true residual retardation is 5λ , the black band, as previously stated, is

one band below the neutral band in the margins, giving an apparent residual retardation of -1λ . Beyond this it was impossible to go as the celluloid developed a crack.

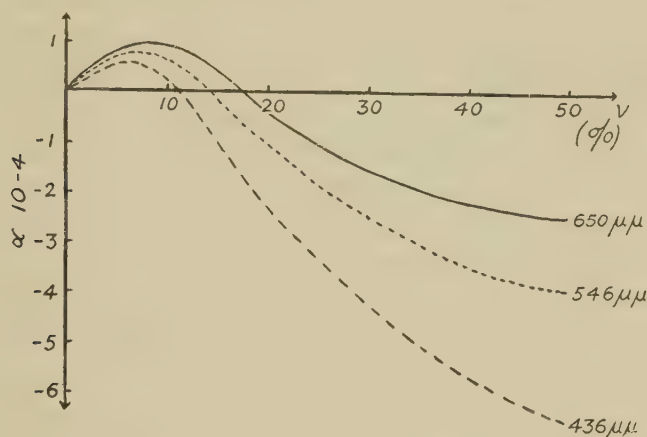


Fig. 5.

It will be seen that curve III resembles in its general features those given by Wächtler (1), and reproduced in fig. 5 for comparison. Interpolating between Wächtler's curves it is found that, if he had used sodium light, the point where his curve would have cut the elongation axis corresponds to an elongation of 15 per cent. Curve III, fig. 3, cuts the elongation axis at an elongation of 17 per cent. This agreement appears striking and it seems difficult to resist the conclusion that both Ambronn and Wächtler may have been misled by this singular change in the dispersion into a wrong estimate of their zero, and consequently of the whole double refraction. Of course this is only a tentative explanation of the discrepancy mentioned at the beginning of this article, and until definite details are known about the method used by Wächtler to determine the residual double refraction, it is not possible to say whether this explanation is correct.

There is, however, one other possibility which ought to be mentioned. It may be that the material used by Ambronn and Wächtler was entirely different in its photo-elastic properties from the xylonite used in our experiments; but, in that case, since xylonite is also the material used by Coker and Filon and Jessop in their researches, the criticisms by Wächtler on these investigators would hardly be to the point. However, it seems very difficult to admit that, in such closely related materials, the photo-elastic behaviour should be so widely divergent as to exhibit, in one case, what would be a unique anomaly, while

giving a comparatively normal variation of the stress-optical coefficient in the other.

12. It was found impossible with xylonite to reach a permanent elongation of 50 per cent., the highest obtained by Wächtler with his celluloid. Different specimens of xylonite all fractured as soon as permanent elongations of 35 to 40 per cent. were exceeded. The author is indebted to Dr. Wächtler for the information that his specimens received their permanent stretches with frequent interruptions, and that heat was applied during the process. As heating alone, however, has been found to affect the stress-optical properties of celluloid, it was considered inadvisable to enhance the elongations in this manner, on account of the additional complications to be expected.

13. It would appear from the experiments described above that Ambronn and Wächtler's conclusion, that the double refraction in celluloid is reversed when the permanent strain is increased beyond a certain limit, is not confirmed, but that the law of dispersion of double refraction in this material is profoundly affected by overstrain. As has been mentioned above, this point is being studied quantitatively.

The author's thanks are due to Prof. L. N. G. Filon and to Messrs. H. T. Jessop and F. C. Harris, of the Department of Applied Mathematics and Mechanics, University College, London, for their valuable suggestions and criticisms during the course of this investigation.

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*The Conductivity of Uni-univalent Salts in Methyl Alcohol
at 25° C.*

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§ 1. *Introduction.*

The physical properties of solutions of electrolytes in non-aqueous solvents have been investigated in the past by a number of workers, but until recently the work in this field has been characterised to some extent by lack of accuracy and of co-ordination. The need for accurate experimental work in this direction is clear when it is realised that modern theories of the behaviour of electrolytes in solution are based almost entirely on data obtained for solutions in water. It is probable that a more complete understanding of the nature of solutions can come only through experimental work extending over a range of solvents: the peculiar properties of water as a solvent have tended hitherto to obscure many of the fundamental difficulties of the problem by cloaking them in the garb of simplicity.

The work which forms the substance of this paper was undertaken with a view to obtaining some systematic data for the electrical conductivity of dilute solutions of uni-univalent salts in a non-aqueous solvent, of an accuracy comparable with that of Kohlrausch and his co-workers in the case of aqueous solutions. The choice of methyl alcohol as a solvent was governed by the fact that it is most closely allied to water in type, and is experimentally well suited for such an investigation.

The immediate purpose of the work was to test the applicability to methyl alcohol of two laws known to hold for solutions of similar salts in water; the first, the Kohlrausch law of the independent mobility of ions at infinite dilution (1), and the second, the empirical relation found by Kohlrausch for

dilute aqueous salt solutions connecting the equivalent conductivity and the concentration, namely :—

$$\Lambda_0 - \Lambda_c = x\sqrt{C},$$

where Λ_0 Λ_c are the equivalent conductivities at infinite dilution and at concentration C respectively. This equation was used latterly by Kohlrausch (2) to express his results in dilute solution, and has recently received theoretical support in an important paper by Debye and Hückel (3), to which further reference will be made. It may be stated that complete confirmation of the validity of both these laws has been obtained, for all the cases which have been examined. With regard to the measurements of conductivity in methyl alcohol made by previous workers it will be sufficient to say that, in those cases where a comparison of results is possible, the agreement is not satisfactory. The most reliable work in this field is probably that of Goldschmidt (4), whose results for sodium chloride are in general agreement with ours, although at high dilutions his curve rises more steeply.

In any work on solutions the value of the results will depend ultimately on the purity of the solvent. In the case with which we are concerned, the most insidious impurity is water. It has been observed (5) that the presence of 0.1 per cent. of water increases the viscosity of methyl alcohol by 0.4 per cent. approximately, and, therefore, lowers the specific conductivity of a dilute salt solution by about the same amount. Accordingly, if the measurements of conductivity are to be accurate to 0.1 per cent., the amount of water in the alcohol must not exceed 0.025 per cent. It is doubtful whether all previous workers have paid sufficient attention to this point.

The Ostwald-Arrhenius method of measuring conductivity is well known : a salt solution is placed in the conductivity cell and its resistance is measured ; then by successive withdrawals of solution and addition of solvent in volume pipettes, a series of values of conductivity over a range of concentration is obtained. This method is open to the objection that it is not possible to be certain of the proportion of the total conductivity due to the solvent alone at each stage. It is specially unsuited for use with so volatile a solvent as methyl alcohol, owing to the impossibility of preventing evaporation losses during the manipulation. Moreover, any error in the calibration of the pipettes will be cumulative. For these three reasons the errors of a series of measurements carried out in this way will accumulate as the concentration decreases, and in extreme cases an entirely false value for the change of conductivity with decreasing concentration will be obtained.

The errors introduced by the faulty or inadequate application of the solvent correction have led some authors to assume that there is a genuine maximum in the conductivity-concentration curve in the region of great dilution. The occurrence of such phenomena is most common in the cases where there is possibility of chemical reaction between the solute and the solvent impurity. This point is illustrated by the values for the conductivity of silver nitrate in methyl alcohol obtained by Getman and Gibbons (6), with which may be compared the results given in this paper.

In order to reduce to a minimum the errors arising from the sources enumerated above, the Ostwald-Arrhenius method of dilution has not been employed. In its place was used a method, suggested by Whetham (7), in which to a known volume of pure solvent are added successive portions of salt solution from a weight pipette. Under these conditions the solvent conductivity is measured *in situ* and is therefore accurately known, and the concentration errors due to manipulation are much reduced, with the result that the measurements in dilute solution are relatively more reliable than those obtained by the dilution method. It should be mentioned that almost all previous workers, including Goldschmidt, have used the Ostwald-Arrhenius method in investigating conductivity in methyl alcohol.

The precautions which have been adopted in order to ensure accuracy are, in the first place, the use of methyl alcohol of great purity and low specific conductivity, and in the second the use of a method of procedure which involves the smallest risk of introduction of concentration errors through evaporation or contamination. The range of concentration over which the measurements have been made is from N/500 to N/10,000 approximately.

§ 2. *Experimental Procedure.*

Preparation of the Solvent.—The pure methyl alcohol used in these experiments was prepared exactly as described by Hartley and Raikes (5), and was tested for impurities in the way indicated in that paper. It was found that the final conductivity was appreciably lowered by carrying out the preliminary distillations from a little sodium methoxide, and in the later experiments this was always done. The specific conductivity of the alcohol used in each experiment is stated in the tables.

Measurement of Resistance.—Resistances were measured by means of an alternating current, with a telephone as the indicating instrument. The bridge assembly was of the normal Wheatstone type, with a cylindrical bridge drum which could be read to 0.01 per cent. of its length. The resistances

were of the special non-inductive type, and were standardised by the tare-box method against 10, 100, and 1,000-ohm coils certified by the N.P.L. All precautions necessary to ensure accuracy were taken in accordance with the best practice. The alternating current was provided by a small finely-tuned coil, as recommended by Kohlrausch, and also by a Siemens-Schuckert alternator: the two gave identical results, but latterly the alternator was preferred as being less troublesome to keep in order than the coil. In the measurement of the resistance of the pure solvent, direct current and a galvanometer were employed on certain occasions when the resistance was very high.

Preparation of the Salt Solutions.—The salts were dried and weighed in a small platinum crucible, enclosed for the weighing in a well-stoppered bottle, with a similar bottle as counterpoise. The crucible and salt were transferred afterwards to a wide-necked stoppered flask and weighed, the amount of pure alcohol needed to give a solution approximately thirtieth-normal was added, and the whole was weighed once more. The weight pipette was filled direct from this flask, the risk of loss of solvent by evaporation being thereby reduced to a minimum. The solutions were made up with the same sample of alcohol that was to be used for filling the cell. All weighings were reduced to a vacuum standard.

The small solubility in methyl alcohol of the nitrates of potassium, rubidium, and caesium necessitated the use of a somewhat more dilute stock solution for the weight pipette (about N/70).

The Conductivity Cell.—The cell used throughout this work was identical with that described by Hartley and Barrett (8), except for the fact that it was flat-bottomed. It consists of a flask of borosilicate glass, of 250 c.c. capacity, with an externally ground cap through which are fused two tubes carrying the electrodes. The latter are coated with grey platinum, and are placed vertically in the cell. The salt solution is added through a small cap on the main cap, while a slow stream of pure air is passed into the cell, through a three-way tap also attached to the main cap, to prevent the absorption of atmospheric impurity. After the addition the liquid is stirred by vigorously rotating the main cap; this can be continued if desired during the reading of the resistance. A diagram of the cell, together with a description of the exact method of carrying out a run, is given in the above-mentioned paper. It was usual to make six or seven additions in each run.

The weight pipette, which had a capacity of 10 c.c., was fitted with a small tap lubricated by a paraffin and vaseline mixture, carefully purified and boiled out with methyl alcohol; its stem was drawn out to a fine point,

which was covered by a small cap while the pipette was resting on the balance. The top of the pipette was fitted with a ground-on glass cap carrying a short fine capillary tube. By dipping the tip of the pipette beneath the surface of the salt solution contained in the stoppered flask, and applying suction to the capillary, the pipette could be filled without risk of loss of solvent by evaporation. The cap was not removed during a run.

Temperature Control.—The cell was immersed in an electrically heated bath whose temperature was kept constant to 0.01° C. by means of a Lowry-type spiral thermo-regulator, filled with pure benzene and distilled mercury. The regulator and relay were so placed as to receive some vibration from the motor which drove the propeller stirring the bath.

In order to prevent condensation of the solvent on the inside of the cell cap, which was apt to occur if the air above the bath was several degrees cooler than the bath itself, the room was kept at a temperature of about 22° to 23° C.

Calculation of Concentrations.—All concentrations C are expressed in gram equivalents per litre of solution *in vacuo* at 25° C. In the first instance, concentrations are known in weight normalities; to convert to volume normality it has been assumed that the density of the solution is sensibly the same as that of the pure solvent. At the highest concentrations reached this assumption involves no error greater than one part in five thousand. The density of methyl alcohol has been taken as 0.7864 at 25° C. (5).

The solvent correction has in each case been applied by subtracting the conductivity of the pure solvent measured at the beginning of the run from the total conductivity at each concentration. With alcohol whose specific conductivity is 0.05 reciprocal megohms, the proportion of the total conductivity of a $N/10,000$ solution due to the solvent alone is roughly $1/300$, so that a small error in measuring the solvent conductivity will be relatively unimportant.

The Cell Constant.—This value has been determined at frequent intervals during the work, and no perceptible variation has been detected. The measurements have been made over the same range of concentration, and under the same conditions as the experiments on methyl alcohol, by carrying out a series of determinations with water in the cell and aqueous potassium chloride in the weight pipette. The values for the specific conductivity of potassium chloride solutions have been obtained by linear interpolation of Kohlrausch and Maltby's values (9) for the equivalent conductivity at 18° C., with the aid of the equation

$$\Lambda_c = 129.91 - 80.75\sqrt{C}.$$

The agreement between the original observed values and those calculated from this equation is shown below :—

$100\sqrt{C}$.	Λ_c observed by Kohlrausch (mean)	Λ Calculated.	Diff. $\Lambda_{\text{obs.}} - \Lambda_{\text{calc.}}$
1.014	129.045	129.092	-0.047
1.433	128.755	128.754	0.001
2.262	128.085	128.083	0.002
3.191	127.310	127.332	-0.022
4.490	126.290	126.286	0.004

It is clear that these figures justify the procedure adopted in obtaining the equivalent conductivity below N/500. The specific conductivity is calculated from the appropriate value of the equivalent conductivity and compared with the conductivity observed in the cell, and the cell constant obtained by division. In the fifth standardisation the specific conductivity at 25° C. was obtained from that at 18° with the aid of Déguignes coefficients.

In view of the fact that the cell constant controls the absolute value of conductivity measurements, the actual method of calculating this value has been given. The recent work of Parker (10) on the re-determination of the absolute values for the specific conductivity of potassium chloride solutions, indicates that at N/10 and N/100 the values of Kohlrausch are not quite correct. Should the values below N/500 prove also to be incorrect, the appropriate correction can easily be made if the method by which a cell constant has been determined be known.

The values for the cell constant obtained are tabulated below :—

Date.	$C \times 10^4$.	Cell Constant.	Mean of Each Series.
A. Oct., '23	12.053	0.034045	0.03405 ₅
(At 18°)	20.387	0.034063	
B. Nov., '23	3.896	0.034063	0.03405 ₆
(At 18°)	14.253	0.034048	
C. Nov., '23	6.069	0.034064	0.03405 ₄
(At 18°)	9.921	0.034054	
	13.714	0.034045	
D. Feb., '24	7.280	0.034057	0.03405 ₈
(At 18°)	12.763	0.034049	
	17.615	0.034069	
E. Mar., '25	1.556	0.034047	0.03405 ₂
(At 25°)	3.394	0.034049	
	5.937	0.034060	

The value used throughout in the calculations is 0.03405₅.

Purity of Salts.—In the majority of cases the salts used were Merck's or Kahlbaum's purest products, further purified by re-crystallisation followed by centrifuging. The cæsium chloride (kindly supplied by A. C. G. Egerton), the lithium salts, and the rubidium nitrate were found spectroscopically to be free from other metals. The rubidium chloride was prepared from the nitrate by continued evaporation with constant boiling hydrochloric acid. One sample of silver nitrate was prepared from pure silver, the other by re-crystallisation of the commercial product. It may be mentioned that methyl alcohol is a convenient solvent for re-crystallising salts which are rather soluble in cold water and of which only a small quantity is available. The potassium fluoride and sodium bromide were known to contain small quantities of impurities from which they could not be purified by crystallisation; the values for these salts are therefore only approximate.

Accuracy of the Results.—It is estimated that the final values for the equivalent conductivity at infinite dilution are, with the two exceptions just mentioned, accurate to within one part in a thousand. The agreement between individual runs is often greater than this, as may be seen from the tabulated results which follow. In the following tables each experiment was carried out with an independent salt solution in the weight pipette, using, where possible, samples of salt of different origin for making up the solutions. The salts which have been examined are the chlorides and nitrates of the alkali metals, potassium bromide, iodide and fluoride, silver nitrate and sodium bromide.

§ 3. Tabulated Results of Conductivity Measurements.

Explanation of the Tables.—As stated before, the variation of equivalent conductivity with concentration can be expressed in the form $\Lambda_0 = \Lambda_c + x\sqrt{C}$, where C is the concentration, in this case expressed in gram-equivalents per litre of solution at 25° C., and x is the slope of the $\Lambda_c/\sqrt{C}$ plot.

At the side of each table are given the values of Λ_0 and x for each salt, obtained by taking the best mean value of the different series with each salt, and in *Column 1*, the specific conductivity (k) of the pure solvent in reciprocal megohms; *Column 2*, the value of $C \times 10^4$; *Column 3*, the value of $100\sqrt{C}$; *Column 4*, the observed equivalent conductivity (Λ_c); *Column 5*, the value of (Λ observed — Λ calculated), where the latter is the value obtained from $\sqrt{C}$, Λ_0 , and x by substitution in the general equation.

The value of the differences (D) in column 5 show the conformity of the results to the square-root law. The letters *a*, *b*, *c* refer to the independent series of experiments with each salt.

	k .	$C \times 10^4$.	$100\sqrt{C}$.	Λ_c .	D.
<i>Lithium chloride.</i>					
Series <i>a</i>	0.240	2.7370	1.654	87.24	+0.03
		4.7612	2.183	86.01	-0.02
		6.5055	2.551	85.16	-0.03
		9.8915	3.145	83.84	-0.03
		17.9420	4.236	81.42	-0.01
Series <i>b</i>	0.340	2.0873	1.445	87.60	-0.07
		4.2725	2.067	86.30	+0.01
$\Lambda_0 = 90.91$		6.6060	2.571	85.19	+0.02
		9.1401	3.024	84.15	+0.01
$x = 224$		12.4870	3.534	83.05	+0.04
		(22.2150)	4.714	80.75	+0.39)?
<i>Sodium chloride.</i>					
Series <i>a</i>	0.500	1.4764	1.211	94.24	+0.06
		2.7933	1.671	93.19	+0.06
		4.2550	2.063	92.16	-0.06
		7.2393	2.691	90.76	-0.02
		10.0790	3.175	89.70	+0.03
		18.7080	4.325	87.04	+0.02
Series <i>b</i>	0.110	1.1232	1.066	94.44	-0.08
		2.4803	1.574	93.23	-0.02
$\Lambda_0 = 96.97$		4.0090	2.002	92.37	+0.01
		6.9760	2.641	90.80	-0.09
$x = 230$		9.8350	3.136	89.74	+0.00
		18.8670	4.344	86.99	+0.01
<i>Potassium chloride.</i>					
Series <i>a</i>	0.041	1.5917	1.261	101.80	-0.02
		3.1766	1.782	100.41	+0.01
		5.2791	2.297	99.01	+0.06
		8.0981	2.846	97.62	+0.03
		11.4700	3.387	96.24	± 0.00
		14.8460	3.853	95.02	+0.02
		20.3970	4.516	93.33	-0.03
Series <i>b</i>	0.062	1.0951	1.047	102.25	+0.09
		2.3289	1.526	101.15	-0.06
		4.0912	2.023	99.76	+0.03
		6.1982	2.490	98.56	+0.01
		8.5183	2.919	97.45	± 0.00
		14.4200	3.797	95.16	+0.01
Series <i>c</i>	0.035	1.1212	1.059	102.35	+0.04
		2.2465	1.499	101.27	+0.12
$\Lambda_0 = 105.07$		4.2560	2.063	99.62	-0.07
		6.2920	2.508	98.55	+0.06
$x = 261$		8.8575	2.976	97.28	-0.01
		15.9640	3.995	94.54	-0.11
<i>Rubidium chloride.</i>					
Series <i>a</i>	0.034	2.1191	1.456	104.57	-0.05
		3.8715	1.968	103.11	-0.02
$\Lambda_0 = 108.65$		5.9926	2.448	101.72	+0.01
		7.9862	2.826	100.60	+0.06
$x = 281$		10.5470	3.248	99.50	-0.04
		13.4300	3.665	98.45	± 0.00
		17.0090	4.124	97.10	± 0.00

	<i>k.</i>	$C \times 10^4$.	$100\sqrt{C}$.	Λ_c .	D.
<i>Cæsium chloride.</i>					
Series <i>a</i>	0.095	1.3395	1.158	110.00	+0.25
		2.7626	1.662	108.73	± 0.00
		4.6383	2.154	107.32	+0.03
		6.3141	2.513	106.24	± 0.00
		9.0880	3.015	104.82	+0.05
		15.0370	3.878	102.26	+0.01
Series <i>b</i>	0.071	1.6235	1.274	109.90	+0.03
		3.5656	1.888	108.10	+0.03
$\Lambda_0 = 113.60$		5.6307	2.373	106.61	-0.04
		8.2400	2.871	105.20	+0.03
$x = 293$		11.5950	3.405	103.57	-0.05
		16.4330	4.054	101.72	-0.01
<i>Lithium nitrate.</i>					
Series <i>a</i>	0.220	1.7422	1.320	96.89	-0.05
		3.2451	1.801	95.62	-0.13
		4.7910	2.189	94.65	-0.13
		6.6186	2.573	93.66	-0.16
		9.7383	3.121	92.32	-0.13
		14.8170	3.849	90.57	-0.06
Series <i>b</i>	0.047	1.5988	1.265	96.96	-0.13
		3.2255	1.796	95.77	+0.02
$\Lambda_0 = 100.25$		5.5701	2.360	94.34	± 0.00
		7.5545	2.749	93.44	+0.06
$x = 250$		10.8960	3.301	92.04	-0.03
		19.3080	4.394	89.58	+0.28
<i>Sodium nitrate.</i>					
Series <i>a</i>	0.100	1.8470	1.359	102.52	-0.04
		3.9990	2.000	100.69	-0.02
		5.9790	2.445	99.44	+0.03
		9.3480	3.057	97.66	+0.01
		12.0660	3.473	96.41	-0.03
		17.3940	4.170	94.45	+0.02
Series <i>b</i>	0.410	2.3660	1.538	102.07	+0.05
		4.0346	2.009	100.69	+0.02
$\Lambda_0 = 106.45$		6.5330	2.556	99.10	+0.01
		9.8740	3.145	97.36	-0.03
$x = 288$		16.2800	4.035	94.82	± 0.00
<i>Potassium nitrate.</i>					
Series <i>a</i>	0.090	0.9731	0.987	110.93	-0.23
		1.8169	1.348	109.97	+0.06
		3.0214	1.738	108.63	+0.08
		4.8517	2.203	107.06	+0.09
		9.6292	3.103	103.94	+0.07
Series <i>b</i>	0.110	1.4304	1.196	110.25	-0.19
		2.4853	1.576	109.01	-0.11
$\Lambda_0 = 114.55$		4.0050	2.001	107.61	-0.05
		5.9341	2.436	106.09	-0.09
$x = 344$		8.1301	2.851	104.66	-0.07
		11.2266	3.351	102.99	-0.03

	<i>k.</i>	$C \times 10^4.$	$100 \sqrt{C}.$	$\Lambda_c.$	D.
<i>Rubidium nitrate.</i>					
Series <i>a</i>	0.160	1.1220	1.059	114.15	−0.20
		2.1627	1.471	112.84	−0.03
		3.4020	1.844	111.57	−0.02
		4.9996	2.236	110.20	±0.00
		7.2403	2.691	108.61	+0.03
		10.2150	3.195	106.81	±0.00
		13.5100	3.676	105.06	−0.04
Series <i>b</i>	0.140	1.3152	1.147	113.88	−0.20
		2.3368	1.529	112.71	−0.01
$\Lambda_0 = 118.15$		3.5320	1.879	111.41	−0.07
		5.5402	2.354	109.74	−0.05
$x = 355$		7.7380	2.782	108.30	+0.07
		11.8910	3.448	105.87	−0.05
<i>Cæsium nitrate.</i>					
Series <i>a</i>	0.016	0.6104	0.781	120.26	+0.26
		1.1782	1.085	118.88	−0.04
		1.8086	1.345	117.88	+0.03
		2.9550	1.719	116.36	−0.07
		4.1502	2.037	115.23	+0.00
		5.9400	2.437	113.70	−0.02
Series <i>b</i>	0.015	0.5035	0.709	119.89	−0.37
		1.0353	1.017	119.11	+0.02
$\Lambda_0 = 122.95$		1.6540	1.286	118.08	+0.01
		3.2138	1.793	116.16	+0.01
$x = 379$		4.5429	2.131	114.84	−0.03
		6.1957	2.489	113.48	−0.03
<i>Silver nitrate.</i>					
Series <i>a</i>	0.110	1.7440	1.321	106.51	−0.48
		3.4820	1.866	104.53	+0.00
		5.1645	2.273	102.75	+0.05
		7.2150	2.686	100.90	+0.05
		9.6510	3.106	99.01	+0.06
		16.1670	4.021	94.85	+0.10
Series <i>b</i>	0.120	1.5840	1.259	106.55	−0.85
		3.4580	1.860	104.30	−0.27
$\Lambda_0 = 112.95$		5.5080	2.347	102.28	−0.17
		8.0890	2.844	100.15	+0.08
$x = 451$		10.6060	3.257	98.18	+0.04
		16.0530	4.007	94.83	+0.03
<i>Potassium bromide.</i>					
Series <i>a</i>	0.041	1.4643	1.210	106.14	+0.01
		2.7950	1.671	104.99	+0.02
		5.0406	2.224	103.48	+0.01
		7.2425	2.691	102.27	−0.03
		10.6330	3.260	100.83	+0.02
		18.3780	4.287	98.25	+0.12
Series <i>b</i>	0.048	1.2754	1.129	106.43	±0.00
		2.4162	1.554	105.22	−0.06
$\Lambda_0 = 109.35$		4.5351	2.130	103.77	±0.00
		6.4352	2.537	102.71	±0.00
$x = 262$		8.9501	2.992	101.53	+0.02
		16.2200	4.027	98.74	−0.06

	k .	$C \times 10^4$.	$100 \sqrt{C}$.	Λ_c .	D.
<i>Potassium bromide.</i>					
Series c	0.041	0.8058	0.898	106.99	± 0.00
		3.2059	1.790	104.67	+0.01
		5.5445	2.355	103.11	-0.07
		7.9683	2.823	101.98	+0.02
		10.7000	3.263	100.75	-0.06
		15.0940	3.885	99.25	+0.05
<i>Potassium iodide.</i>					
Series a	0.021	1.2595	1.122	111.81	-0.05
		2.5020	1.582	110.73	+0.04
$\Lambda_0 = 114.75$		4.2636	2.065	109.44	± 0.00
		5.8000	2.408	108.57	+0.02
		8.0458	2.837	107.45	+0.02
$x = 260$		13.8724	3.725	105.16	+0.04

In addition, the following approximate values for the conductivity of potassium fluoride and sodium bromide have been obtained :—

Potassium fluoride .. $\Lambda_0 = 94.0$ $x = 236$

Sodium bromide .. $\Lambda_0 = 101.5$ $x = 240$

The individual figures in each case agree closely with those calculated from the square-root formula.

Discussion of Results.—It will have been seen that in certain cases the conductivity calculated from the square-root formula is higher than that actually observed for the most dilute solution of a run, the discrepancy being shown in the fifth column of the tables. In the authors' opinion this discrepancy is due rather to experimental error than to the failure of the law to hold in very dilute solutions, and may be explained on the basis of error in the solvent correction or of absorption of the salt by the electrodes. Apart from these values, the conformity to the square-root law is very close for concentrations lower than $N/500$. A few measurements in more concentrated solution have shown that in the neighbourhood of this point the law ceases to hold, the behaviour being similar to that in water. For concentrations between $N/500$ and infinite dilution the equivalent conductivity may be calculated accurately from the general equation, and conductivities at round concentrations can, if required, be obtained at once with the aid of the appropriate constants which are summarised in Table I below. The values for hydrochloric acid, ammonium chloride, and sodium methoxide have been obtained in this laboratory by W. F. Wynne-Jones (11), and that for sodium perchlorate by F. A. Philbrick, and are included, with the authors' consent, for purposes of comparison.

Table I.—Values of Λ_0 and x in Methyl Alcohol at 25° C.

Salt.	Λ_0	x	Salt.	Λ_0	x
LiCl	90.90	224	LiNO ₃	100.25	250
NaCl	96.95	230	NaNO ₃	106.45	288
KCl	105.05	261	KNO ₃	114.55	345
RbCl	108.65	281	RbNO ₃	118.15	355
CsCl	113.60	293	CsNO ₃	122.95	379
KF	94.0	236	AgNO ₃	112.95	451
KBr	109.35	262	NaBr	101.5	240
KI	114.85	260	NaOMe	98.40	222
NH ₄ Cl	111.00	265	NaClO ₄	115.10	280
HCl	193.5	368			

§ 4. *Ionic Mobilities at Infinite Dilution.*

That Kohlrausch's law of independent mobility holds within the limits of experimental error may be seen from the following table, which gives the differences in the values of Λ_0 for the nitrates and chlorides of five metals :—

Table II.—Test of the Law of Independent Mobility.

Cation.	Li	Na	K	Rb	Cs
Λ_0 nitrate — Λ_0 chloride	9.35	9.50	9.50	9.50	9.35

It is therefore possible to arrive at the individual values of the mobilities, when once the value of Λ_0 and the transport numbers of any one of the salts concerned have been obtained. In view of the fact that no reliable data for transport numbers of salts in methyl alcohol at high dilution are available, it has been decided to make use of the transport number of the hydrogen-ion in hydrogen chloride obtained by G. Nonhebel (12) from a series of measurements of the E.M.F. of concentration cells in methyl alcohol between 0.0045 and 0.155 N. (An account of this work is being published elsewhere.) The value adopted is $n_c = 0.735$ at infinite dilution. Combining this with the value of Λ_0 for hydrochloric acid (Wynne-Jones, *loc. cit.* (11)) we arrive at the mobility values given in the first column of the following table. (The letter l is used always to denote the mobility of a single ion.)

The figures in the third column of the following table are the values of the mobilities in water at 25° C., calculated from Kohlrausch's data (13), and those in the fourth column the value of the ratio of the mobility in MeOH to the mobility in water. It is interesting to note that in methyl alcohol, as in water, the mobilities of the ions of the alkali metals increase with increasing

Table III.—Ionic Mobilities in Methyl Alcohol at 25° C.

Ion.	l_{MeOH}	$l_{\text{H}_2\text{O}}$	$\frac{l_{\text{MeOH}}}{l_{\text{H}_2\text{O}}}$	Ion.	l_{MeOH}	$l_{\text{H}_2\text{O}}$	$\frac{l_{\text{MeOH}}}{l_{\text{H}_2\text{O}}}$
Li	39.6	39.6	1.00	F	40.2	54.4	0.74
Na	45.7	50.9	0.90	Cl	51.3	75.4	0.68
K	53.8	74.4	0.72	Br	55.5	77.5	0.71
Rb	57.4	77.6	0.74	I	61.0	76.0	0.81
Cs	62.3	78.1	0.80	—	—	—	—
—	—	—	—	—	—	—	—
Ag	52.2	63.0	0.83	NO ₃	60.8	70.8	0.85
NH ₄	59.8	73.9	0.81	ClO ₄	69.4	76 ?	0.90
H	142.2	349	0.41	OMe	52.7	(OH) 196	—

atomic number and atomic volume, but in methyl alcohol the rise is more regular. In the case of the halogens, the mobilities in methyl alcohol rise regularly with atomic number, but in water chlorine, bromine, and iodine have nearly the same mobility, the value for bromine being slightly the highest.

Column 4 of Table III shows clearly that the ratio of the mobilities in the two solvents varies from ion to ion, indicating that there is no simple relation between them. If the motion of the ions is in accordance with Stokes' law, and the ions are the same size in both solvents, the value of the product (mobility $\times$ viscosity (η_0) of the solvent) should be the same for any single ion in each solvent, or the value of $\frac{l_{\text{MeOH}}}{l_{\text{H}_2\text{O}}}$ should be equal to $\frac{\eta_{\text{H}_2\text{O}}}{\eta_{\text{MeOH}}} = 1.64$ at 25°.

The values of the ratio of the mobilities in column 4 show that the relative speeds of the ions in methyl alcohol are smaller than would be expected from its low viscosity. This can be explained on the solvation theory by supposing that the ion-solvent complexes are larger in methyl alcohol than in water. An alternative explanation was given by Born, who suggested that the resistance to ionic motion is due in part to the bulk viscosity of the solvent, and in part to the electrical interaction between ions and solvent molecules. On either hypothesis the larger the ion the nearer will the ratio of the mobilities approach the value 1.64. Walden and also Wynne-Jones (11) have demonstrated by experiment that this does occur in the case of large organic ions.

§ 5. The Variation of Equivalent Conductivity with Concentration.

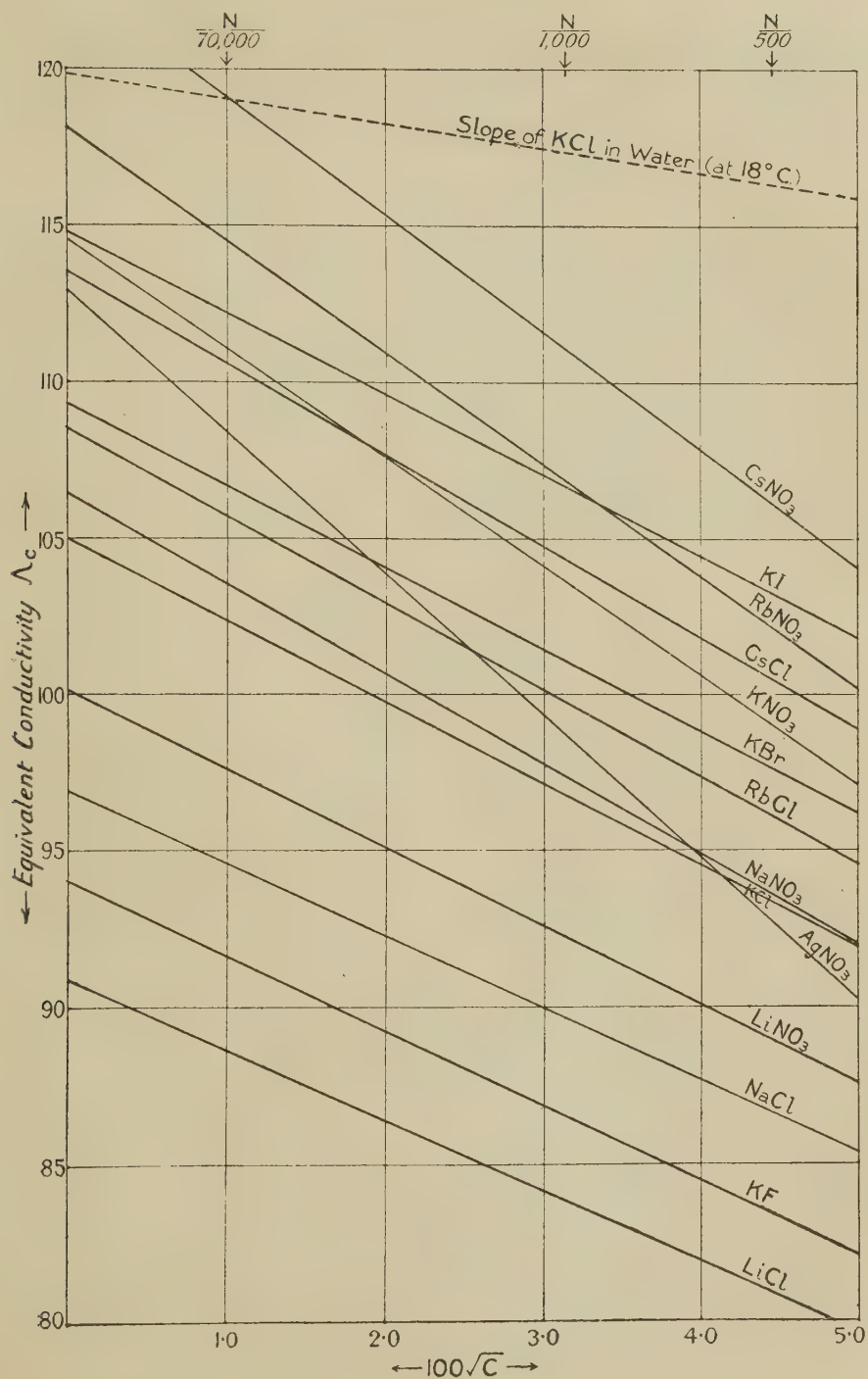
It has already been pointed out that the variation in the equivalent conductivity with concentration both in water and methyl alcohol can be represented by the equation $\Lambda_c = \Lambda_0 - x\sqrt{C}$.

In the accompanying diagram the values of Λ_0 are plotted against the square root of the equivalent concentration, and if the graphs are compared with a similar diagram for aqueous solutions it will be seen that the slopes of the lines are about four times as steep in methyl alcohol as in water, and that, whereas in water they are approximately parallel for the salts examined, in methyl alcohol there are more definite differences in slope.

The values of x in Table I show that both with the chlorides and with the nitrates of the alkali metals there is an increase in slope in passing from lithium to caesium, and that as a group the nitrates have a steeper slope than the chlorides. The slope of silver nitrate is very much steeper than that of any other uni-univalent salt which has been examined, though in water the value is much the same as that of the alkali nitrates. The slope of the lines in methyl alcohol evidently depends on both the ions present, and the contrast between the behaviour in this solvent and water is a further instance of Hantzsch's observation that the individual differences between various electrolytes is much more marked in non-aqueous solvents than in water, in which the properties of electrolytes seem to depend more exclusively on the valency types of the constituent ions.

On the classical dissociation theory the fall in conductivity with increasing concentration was supposed to be due mainly to the decrease in the degree of ionisation of the solute; the modern theory, which is based on the assumption of complete dissociation, attributes this fall to the electrical forces acting between ions. The treatment of the conductivity problem by Debye and Hückel (3), on the basis of complete dissociation, supposes that as a result of the electrical attraction between oppositely charged ions there is in the immediate neighbourhood of any single ion an excess of ions of opposite charge, just as in the structure of a crystal of sodium chloride.

Owing to the finite time which is necessary for the re-distribution of the ions to take place around an ion that is in motion through the solution ("time of relaxation"), there will always be an excess of ions of opposite sign in its rear, and hence it will be subject to a retardation when moving in an electric field. Further, as the ions of opposite sign are moving in opposite directions and as both are supposed to drag with them a certain amount of solvent, the viscous resistance to the motion of the ion will be greater than if the solvent were simply at rest. Both these effects act in such a way as to reduce the speed of the ions, and both will increase in magnitude as the concentration of the electrolyte increases, and will depend on the valency of the ions and on the dielectric constant of the solvent.



On this theory Debye and Hückel have shown that the magnitude of each of these effects is proportional to the square root of the concentration, and have deduced the following equation for the variation of the equivalent conductivity with concentration, in the case of a uni-univalent electrolyte:—

$$1 - f_{\Lambda} = \frac{\Lambda_0 - \Lambda_c}{\Lambda_0} = [K_1 w_1 + K_2 \cdot b] \sqrt{2C},$$

where the first term, $K_1 w_1$, represents the diminution in conductivity due to the period of relaxation, and the second, $K_2 b$, that due to the electrophoresis of the solvent. w_1 for uni-univalent salts has the value $\frac{1}{2} \left\{ \frac{l_a}{l_c} + \frac{l_c}{l_a} \right\}$ where l_a, l_c are the mobilities of anion and cation. “ b ” is defined as the mean value of the radii of anion and cation.

The terms K_1 and K_2 are numerical quantities depending on the temperature and dielectric constant of the solvent. They may be written in the form

$$K_1 = \frac{\varepsilon \cdot F}{6D \cdot R \cdot T} \sqrt{\frac{4\pi F^2}{D \cdot R \cdot T \times 10^3}},$$

$$K_2 = \sqrt{\frac{4\pi F^2}{D \cdot R \cdot T \times 10^3}},$$

where ε is the charge on an ion, and $F = N\varepsilon$ is the value of the faraday; D is the dielectric constant of the solvent at temperature T , and R is the gas constant per gram-molecule.

Inserting the numerical value of the constants, and taking the value of the dielectric constant of methyl alcohol as 30.3 at 25°, the equation reduces to the form

$$1 - f_{\Lambda} = \{1.146 w_1 + 0.3741 \times 10^8 b\} \sqrt{2C}.$$

The experimental results in this paper are expressed in the form

$$\Lambda_0 = \Lambda_c + x \sqrt{C}, \quad \text{or} \quad 1 - f_{\Lambda} = \frac{x}{\Lambda_0} \sqrt{C},$$

which may be re-written in the form

$$1 - f_{\Lambda} = \frac{x}{\sqrt{2} \Lambda_0} \sqrt{2C}.$$

Combining this with the Debye equation, we arrive finally at the expression

$$b \times 10^8 = \left[\frac{x}{\sqrt{2} \Lambda_0} - 1.146 w_1 \right] \div 0.3741.$$

Table 4 shows that the term $1.146 w_1$ is insufficient to account for the whole decrease in conductivity, and the last column gives the values $b \times 10^8$ calculated from the differences between $\frac{x}{\sqrt{2}\Lambda_0}$ and $1.146 w_1$.

Table IV.

Salt.	$\frac{x}{\sqrt{2}\Lambda_0}$	$1.146w_1$	$b \times 10^8$	Salt.	$\frac{x}{\sqrt{2}\Lambda_0}$	$1.146w_1$	$b \times 10^8$
LiCl	1.744	1.184	1.50	LiNO ₃	1.764	1.251	1.37
NaCl	1.678	1.155	1.40	NaNO ₃	1.914	1.192	1.93
KCl	1.759	1.147	1.64	KNO ₃	2.127	1.155	2.60
RbCl	1.828	1.155	1.80	RbNO ₃	2.127	1.149	2.61
CsCl	1.825	1.169	1.75	CsNO ₃	2.180	1.147	2.76
KBr	1.695	1.147	1.47	AgNO ₃	2.825	1.160	4.45
KI	1.602	1.156	1.19	NaClO ₄	1.737	1.249	1.30
KF	1.768	1.192	1.54	NaOMe	1.596	1.146	1.20
NH ₄ Cl	1.685	1.158	1.41	NaBr	1.672	1.169	1.34

It will be seen that the values of b are all of the order of magnitude of a molecular diameter, and hence it may be said that in methyl alcohol as in water the Debye equation is in approximate agreement with experimental results. However the differences in slope in the conductivity curves for salts with almost the same values for l_a and l_c (see Table III), such as KI, KNO₃, and AgNO₃, are incompatible with the equations, indicating that some minor revision of the theory is necessary.

Debye himself has pointed out that the assumption that the ions obey Stokes' law may not be strictly accurate, and, what is perhaps more important, the assumption that the dielectric constant does not alter with the concentration may not be strictly true even in dilute solution. Redlich (14) has shown that by using a modified form of Stokes' law it is possible to get an exact agreement with experimental results in aqueous solutions; in methyl alcohol, however, his modification of the theory breaks down. An attempt to solve this problem on rather different lines, due to Davies (15), also fails when applied to solutions in methyl alcohol.

Although Debye's equation gives a most valuable indication of the magnitude of $1 - f_A$ in methyl alcohol, it is still impossible to predict the exact value of this quantity from a knowledge of the properties of the solvent and solute.

6. *Summary.*

1. The electrical conductivity between N/10,000 and N/500 of fifteen uni-valent salts in methyl alcohol has been measured at 25° C.

2. Confirmation of the applicability of Kohlrausch's law of the independent mobility of ions has been obtained.

3. It has been shown that Kohlrausch's square-root relation holds good within the range of concentration examined. In this respect the results are in complete accord with Debye's theory of conductivity, but in certain other respects the theory may need some modification.

4. A comparison has been made of ionic mobilities in water and methyl alcohol.

We are indebted to the Government Grant Committee and the Royal Society for a grant which defrayed part of the cost of the apparatus.

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The Arc Spectrum of Palladium, its Zeeman Effect and Spectral Type.

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[PLATES 7 AND 8.]

Introductory.

Palladium is a metal occurring in the eighth group of the periodic table of the elements. Of atomic number 46 and atomic weight 106·7, it is a member of the so-called triad—ruthenium, rhodium, palladium. In the vertical column of the table, palladium occupies a position between nickel and platinum. According to the alternation law governing the multiplicities of terms in the line-spectra of the elements, only odd multiplicities are to be expected in the even groups of the table, and *vice versa*. The numerous spectral regularities which have been discovered in the arc spectrum of iron,*† belong entirely to triplet, quintet, and septet systems. The arc spectrum of cobalt, on the other hand, has been shown by Walters‡ to contain quartets. This would seem to indicate that the present grouping of these elements is erroneous, and that a division should occur between iron and cobalt, and probably also between cobalt and nickel.

The behaviour of elements in the other groups of the table makes it probable that ruthenium and osmium, in the same vertical column, should be in the same group with iron, and that their spectra should be similar and should contain only odd multiplicities. Similarly, rhodium and iridium would be grouped with cobalt, and only terms of even multiplicity should appear in their spectra. The next group would then be nickel, palladium, and platinum, and again odd multiplicities would be expected. An analysis of the spectrum of nickel has been undertaken at the laboratory of the Bureau of Standards in Washington.§ Some photographs of the Zeeman effect of nickel have been made by the present writer, and the patterns observed indicate that the spectrum of nickel contains triplet terms.

* Walters, 'Jour. Opt. Soc. Am.,' vol. 8, No. 2, Feb., 1924.

† Laporte, 'Zeit. f. Physik,' April 19, 1924.

‡ Walters, 'Jour. Wash. Acad. Sci.,' vol. 14, Oct. 19, 1924.

§ A preliminary announcement of results records the discovery of singlet and triplet terms. ('Jour. Wash. Acad. Sci.,' Mar. 4, 1925.)

The present research has been undertaken with the object of providing some of the additional data necessary for the complete classification of the elements of the eighth group. An examination of the arc spectrum of palladium has been made, which has included new measurements of Zeeman effects, and it is believed that the spectral type of the element has been definitely established. The discovery of triplet and singlet terms, as will be shown later, is fully in accord with theory, and serves to confirm the grouping of the elements suggested above.

Preliminary experiments with the Arc Spectrum.

As a source of light for use in making photographs of the arc spectrum an ordinary arc between metallic poles proved very satisfactory. Some use was made of a carbon arc fed with palladium chloride, and for observing the behaviour of the lines under varying conditions of excitation a flame arc was employed. The flame arc was produced by the introduction of sodium chloride or nitrate, in addition to a salt of palladium, between the poles of a carbon arc. For the observation of diffuse lines a vacuum arc was used. An arc between palladium poles *in vacuo* proved troublesome and difficult to maintain. The difficulty was overcome by the use of silver as one of the terminals of the arc. In the region observed the impurity lines due to the silver were easily recognised and caused little inconvenience. Some photographs were taken using a spark in air as a source of light, and in order to eliminate the air lines in the visible region a spark in hydrogen was employed.

Four different spectrographs were used in the investigation. A large glass prism instrument served for the examination of the visible region. In the ultra-violet, use was made of a quartz instrument of Littrow type, and a large quartz spectrograph of ordinary construction. A 10-foot concave grating in an Eagle mounting was also used, and photographs covering the entire observed range of the arc spectrum were taken in the first and third orders of this instrument.

The arc spectrum of palladium consists of a comparatively small number of lines. The strong characteristic arc lines of the element may be easily recognized by their comparatively great intensity and reversed character. The range of wave-lengths covered by the present observations extends from $\lambda 6000$ to $\lambda 2400$. The number of strong arc lines occurring in this region is about 41. Photographs (a), (b) and (c), Plate 7, were taken in the region where the palladium lines are most numerous and of the greatest intensity. These photographs illustrate the reversed character of the lines and their comparative intensities. Most of the strong lines are included in a system of constant

wave-number differences which indicate that definite relations exist between them.

In addition to the strong arc lines just described, a considerable number of very faint lines occur. These weak lines bear no very obvious relations to the strong arc lines just described. With a single exception, discussed in a later section, no significant wave-number differences have been discovered among these lines.

A small number of lines occurring in the arc spectrum of palladium are of different character and constitute a distinct type by themselves. These lines* are of very diffuse appearance when photographed, using a source of light at atmospheric pressure. The two strongest lines of this type, $\lambda 4099$ and $\lambda 4020$, are comparable in intensity to the ordinary arc lines of palladium and generally appear reversed. When photographed with the arc *in vacuo* these lines are reduced to ordinary sharpness and the reversals disappear. Photographs (d) and (e), Plate 7, were taken with the arc in air and the vacuum arc respectively as sources. A comparison of the two photographs illustrates the sharpening of the lines.

In the visible region there are a number of lines which are strong in the arc, but which probably belong to the enhanced line spectrum of palladium. These lines include the well-marked triplet $\lambda 4875\cdot57$, $\lambda 4817\cdot66$, $\lambda 4788\cdot32$, and the group of lines between $\lambda 5100$ and $\lambda 5750$. A comparison of photographs taken with an arc and spark scarcely suffices to indicate the enhanced character of these lines. In photographs taken with a flame arc as a source of light, however, the enhanced lines disappear completely, while true arc lines of the same intensity remain.

The Zeeman Effect.

It has long been known that the same magnetic resolutions were given by lines constituting different members of the same series in a spectrum, and that corresponding lines in the same series of different elements gave Zeeman effects which were identical.† The recent work of Back and Lande‡ has resulted in the formation of a set of empirical rules by means of which the Zeeman pattern may be calculated for a given combination of spectral terms, when the quantum numbers belonging to the terms are known. These rules have been used by

* In Kayser's wave-length tables these are the lines distinguished by the letter U, indicating that they are very diffuse.

† Preston, 'Trans. Roy. Dublin Soc.' (2), vol. 7, p. 7 (1899).

‡ Back and Lande, 'Zeemaneffekt und Multiplettstruktur' (J. Springer, Berlin, 1925).

many observers in the analysis of spectra, and in all known cases reasonably good agreement has been found between the predicted magnetic resolutions and those found by experimental means.

In the present investigation a series of measurements of the magnetic resolutions of palladium lines has been made, with the object of applying the results obtained to determine the structure of its spectrum. With this object in view, measurements of the magnetic resolutions shown by palladium lines have been compared with those found by other observers for lines whose spectral type is known, and in some cases new types of Zeeman effects, calculated from the rules of Back and Lande, have been found to correspond with the resolutions shown by lines in the spectrum of palladium.

A previous measurement of the magnetic resolution of palladium lines was made by Purvis* in 1906. He used as a source of light an ordinary spark in air, and his measurements include most of the strong arc lines of palladium which are dealt with in the present paper. With the exception of those lines which are divided into simple triplets, most of his patterns have been obtained with inadequate resolving power, and the present series of observations has been considered necessary in order definitely to establish the term combinations to which the lines are due.

Experimental Procedure.—The magnetic field was produced with an electro-magnet of horse-shoe type, having arms 8 cm. in diameter. The pole pieces were conical in shape, tapering at an angle of about 60 degrees. The ends of the poles were 6 mm. in diameter. A current of 6 amperes could be passed through the coils of the magnet for an indefinite period without causing them to overheat, and for most of the experiments this strength of current was used. For short exposures the current could be considerably increased, and some photographs were taken using an exciting current of from 8 to 10 amperes. The field strength varied with the current used and the distance apart of the pole pieces. The maximum field obtained was about 32,000 gauss.

The sources of light used to produce the spectrum were, a spark in air, an ordinary arc in air, and an arc *in vacuo*. The spark was produced with a large induction coil, used in connection with a mercury interrupter and a large plate condenser. The electrodes were palladium wires of about 0.5 mm. diameter. The spark was passed in the magnetic field with the pole pieces 2.5 mm. apart. The spark proved satisfactory as a source of light for lines of moderate intensity which were not too readily reversed. In the case of the stronger lines, the components of the Zeeman patterns them-

* 'Proc. Cambridge Phil. Soc.,' vol. 13, p. 326 (1906).

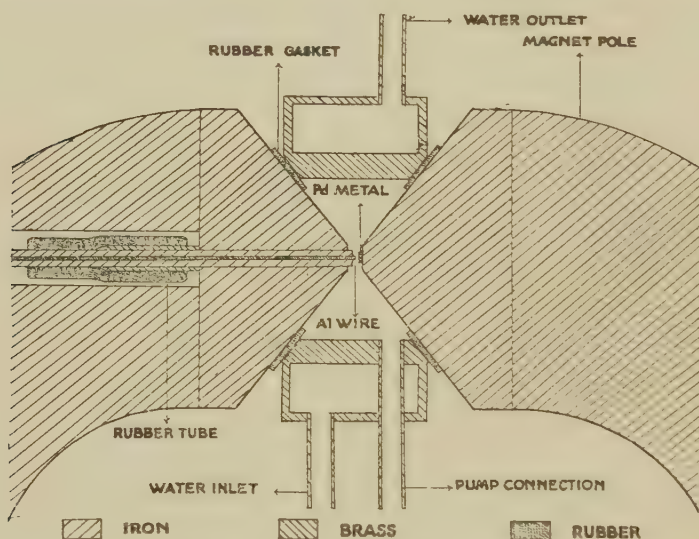
selves appeared reversed and could not be accurately distinguished from one another.

Very good results were secured using an ordinary arc in air as a source of light. The arc has the advantage of requiring very much shorter times of exposure than the spark. In addition to this the conditions under which it is produced may be varied so as to greatly improve the definition obtained. An arc between metallic palladium poles proved to be a very intense source of light, but had the same disadvantage as the spark, *i.e.*, causing reversals in the Zeeman components. This type of arc was used only for the examination of very faint lines. The difficulty due to reversals was largely overcome and at the same time a steadier arc was obtained, by the use of a supplementary substance as the positive pole. In general, aluminium proved to be the most satisfactory for this purpose, though a silver-palladium arc gave better definition in the case of the stronger lines.

In order to establish an arc in the magnetic field without increasing the distance between the poles, the device was adopted of insulating the two arms of the magnet from one another and establishing the arc parallel to the magnetic field between the poles themselves. A small piece of palladium metal was fixed in the centre of one of the pole pieces. The other pole piece had a hole 5 mm. in diameter drilled in the direction of its axis, and through this hole the other terminal of the arc was introduced. When a very powerful source of light was desired this terminal consisted of an aluminium rod, or a brass tube, in the end of which a piece of palladium was fixed. An alternative method was to use a hollow iron rod with an aluminium wire 1.5 mm. in diameter passing through its centre in the direction of its axis. The aluminium wire thus became the positive terminal of the arc, while the iron rod, which was provided with a screw adjustment, acted as a moving magnetic pole and could be moved as close as desired to the opposite pole of the magnet. The use of an iron rod resulted in a stronger and more uniform field. This arrangement necessitated a very feeble arc, in order not to melt the aluminium wire, but it proved sufficiently intense as a source of light for the examination of all but the weakest lines.

The same arrangement was adapted with slight modifications for use with a vacuum arc. The vacuum arc lamp consisted of a tubular brass casting, into the ends of which the conical faces of the magnet pole pieces were fitted. The inside circumferences of the ends of the casting were bevelled at the same angle as the pole pieces, and rubber gaskets were provided at the contacts between the surfaces. The pressure necessary to make the contact air-tight

was provided by the mutual attraction between the poles of the magnet when the field current was turned on. At the point where the rod constituting the positive terminal of the arc passed through the magnet pole, a vacuum-tight connection was provided by a length of rubber tubing suitably connected. The lamp was provided with a water-jacket for cooling and with windows for observing the arc and for allowing the light to be photographed to pass through. The vacuum arc proved more troublesome to operate than the arc in air, but it had the advantage of giving finer definition, particularly in the case of the stronger lines. The sectional diagram illustrates the method of using the arc in the magnetic field, and the construction of the vacuum arc lamp.



The spectrograph used for photographing the Zeeman phenomena was a 10-foot concave grating in an Eagle mounting. Most of the photographs were taken in the third order of this instrument, but some use was made of the overlapping 2nd and 4th-order spectra. A nicol prism served to separate the oppositely polarized components of the Zeeman patterns.

The times of exposure, using the spark as a source of light, varied from 10 minutes to 5 hours, according to the intensity of the lines. Shorter exposures were required with the arc, and most of the photographs were obtained in from 5 to 15 minutes, although an exposure of two hours was required for some of the weakest lines. The vacuum arc lamp was used only for the stronger lines and the photographs were taken with times of exposure of approximately 15 minutes.

Results.—A list of the wave-lengths and wave numbers of palladium lines, with measurements of their Zeeman components, is given in Table I. The wave-lengths quoted are taken from Watts' *Index of Spectra* and are due to Kayser or to Exner and Haschek. The measurements of the Zeeman patterns are decimal fractions of the normal Zeeman resolution, as shown by the separation of components in lines of a singlet system. The numbers in brackets indicate components polarized parallel to the magnetic field. Those components polarized normal to the field are placed outside the brackets. Absence of the brackets indicates that the nicol was not used.

Table I.—Zeeman Effect of Palladium Lines.

λ (Int).	ν .	Zeeman Effect. (Observed.)	Zeeman Effect. (Calculated.)	Combination suggested.
4473·761 (3)	22346·3	0·44, 0·93 , 1·32, 1·79	(0·50, 1·00) 0·50, 1·00, 1·50, 2·00	$p_2 D_2$
4213·115 (5)	23728·8	1·12 (0) 1·06	(0·0 , 0·08, 0·17) 0·92, 1·00, 1·08, 1·17, 1·25	$af_3 D_2$
4170·005 (3)	23974·1	2·50 , 1·48, 0·87 0 1·07, 1·51, 2·49	(0·0 , 1·00) 0·50, 1·50, 2·50	$p_2 d_1$
*4087·518 (4)	24457·8	0·95 (0·40, 0·0, 0·40) 0·95	(0·0, 0·50) 0·50, 1·00, 1·50	$p_1 D_2$
3958·777 (6)	25253·3	1·05 (0) 0·96	(0) 1·00	$D'_2 D_2$
3894·335 (6)	25671·0	1·74 (0) 1·56	(0·0, 0·33, 0·67) 0·67, 1·00, 1·33, 1·67, 2·00	$d'_3 D_2$
3832·410 (5)	26085·7	(0·91) 0·50, 1·43	(1·00) 0·50, 1·50	$p_1 d_1$
3799·332 (6)	26312·9	(0·40, 0·70) 1·11, 1·48, 1·86	(0·33, 0·67) 0·83, 1·17, (1·50, 1·83	$p_2 d_2$
3719·061 (5)	26880·9	1·52, 1·05, 0·52 , 0·0, 0·46, 0·98, 1·47	(0·0, 0·50) 0·50, 1·00, 1·50	$D'_2 d_1$
3690·491 (6)	27089·1	(0·55) 0·55, 1·00, 1·40	(0·33, 0·67) 0·33, 0·67, 1·00, 1·33	$af_2 D_2$
3634·840 (10)	27503·8	1·31 (0) 1·23	(0·0 , 0·17, 0·33) 1·00, 1·17, 1·33, 1·50, 1·67	$p_2 d_3$
3609·678 (10)	27695·3	1·08 (0) 1·02	(0·0 , 0·08, 0·17) 0·92 , 1·00, 1·08, 1·16, 1·25	$af_3 d_2$
3571·305 (6)	27993·1	0·56 (0) 0·48	(0) 0·50	$p_3 d_1$
3553·242 (8)	28135·4	1·23 (0) 1·11	(0·0, 0·08, 0·17) 0·92, 1·00, 1·08, 1·17, 1·25	$bf_3 D_2$
3517·087 (8)	28424·6	1·14 (0) 0·97	(0·0 , 0·33) 0·83 , 1·17, 1·50	$p_1 d_2$
3489·930 (6)	28645·9	1·27 (0) 1·18	(0) 1·00	$aP_1 D_2$
3481·308 (8)	28716·7	1·07 (0) 0·92	(0·0, 0·17) 0·50, 0·67, 0·83	$af_2 d_1$
3460·888 (7)	28886·1	(0·72) 1·39	(0·25, 0·50, 0·75) 0·58, 0·83, 1·08 , 1·33 , 1·58, 1·83	$af_3 d_3$
3441·548 (8)	29048·4	1·11 (0) 1·07	(0·17, 0·33) 0·83, 1·00, 1·17, 1·33	$d'_2 D_2$
3433·582 (6)	29115·9	1·33 (0) 1·29	(0) 1·00	$aP_1 D_2$
3421·368 (9)	29219·7	(0·33) 1·11	(0·17, 0·33) 0·83, 1·00, 1·17, 1·33	$D'_2 d_2$
3404·732 (10)	29362·6	1·21 (0) 1·11	(0·0, 0·08, 0·17, 0·25) 1·00 , 1·08, 1·17, 1·25, 1·33, 1·42, 1·50	$bf_4 d_3$

* Obscured by impurity line.

Table I.—Zeeman Effect of Palladium Lines—(contd.).

λ (Int.)	ν .	Zeeman Effect. (Observed.)	Zeeman Effect. (Calculated.)	Combination suggested.
3373.137 (6)	29637.6	1.55 (0) 1.48	(0.0, 0.17, 0.33) 1.00, 1.17, 1.33, 1.50, 1.83	$d'_3 d_2$
3302.253 (6)	30273.7	(0.36) 0.38, 0.85	(0.50) 0.50, 1.00	$aP_1 d_1$
3287.378 (3)	30410.6	1.76 (0) 1.72	(0.0, 0.33, 0.67) 0.67, 1.00, 1.33, 1.67, 2.00	$D'_2 d_3$
3258.907 (4)	30676.4	1.93, 1.20, 0.66, 0.0, 0.61, 1.13, 1.75	(0.0, 0.67) 0.56, 1.17, 1.83	$d'_2 d_1$
3251.754 (4)	30743.8	(0.32) 0.59	(0.50) 0.50, 1.00	$bP_1 d_1$
3242.824 (9)	30828.5	1.44 (0) 1.27	(0) 1.33	$d'_3 d_3$
3219.088 (2)	31055.9	0.72	(0.50, 1.00) 0.17, 0.67, 1.17, 1.67	$af_2 d_2$
3142.932 (2)	31808.3	1.17 (0) 1.00	—	—
3114.157 (6)	32102.2	1.13 (0) 0.91	(0.0, 0.08, 0.16) 0.92, 1.00, 1.08, 1.16, 1.24	$bf_3 d_2$
3065.425 (5)	32612.8	1.42 (0) 1.27	(0.0, 0.17) 1.00, 1.17, 1.33	$aP_1 d_2$
3028.031 (4)	33015.4	1.21 (0) 1.10	(0) 1.17	$d'_2 d_2$
3021.859 (5)*	33082.8	—	(0.0, 0.17) 1.00, 1.17, 1.33	$bP_1 d_2$
3002.775 (4)	33293.0	0.69	(0.25, 0.50, 0.75) 0.58, 0.83, 1.08, 1.33, 1.58, 1.83	$bf_3 d_3$
2938.550 (0)	34020.6	—	(0.0, 0.50), 0.50, 1.00, 1.50	$d'_1 D^2$
2922.615 (3)	34206.1	1.44 (0) 1.44	(0.0, 0.17, 0.33), 1.00, 1.17, 1.33, 1.50, 1.83	$d'_2 d_3$
2763.199 (3)	36179.4	1.30 (0) 1.30	(0) 1.50	$p_1 S_0$
2631.690 (0)	37987.3	—	(0.0, 0.67), 0.56, 1.17, 1.83	$d'_1 d_2$
2476.509 (3)	40367.5	—	(0) 1.00	$aP_1 S_0$
2447.998 (3)	40837.7	—	(0) 1.00	$bP_1 S_0$

* Obscured by iron impurity.

Table I also contains the term combinations which have been assigned to the lines, with the theoretical Zeeman resolutions corresponding to them.

The value of the normal resolution was calculated from measurements of the resolutions shown by known lines which appeared as impurities in the palladium spectrum. These included the well-known zinc line λ 4680.20, resolution, (0) 2.00; the H and K lines of calcium λ 3933.66 and λ 3968.46, resolutions (0.33), 1.00, 1.66 and (0.66) 1.33, and the silver and copper doublets λ 3280.66, λ 3382.86 and λ 3247.55, λ 3273.97, which gave the same resolutions as the calcium lines. The field strength was calculated from the following formula given by the Lorentz theory of the normal Zeeman effect:—

$$\frac{\Delta\nu}{H} = \frac{1}{12\pi} \cdot e/m \cdot 10^{-10}$$

from which

$$\Delta\nu_{\text{norm.}} = 4.70 \cdot 10^{-5} \cdot H$$

and

$$H = \frac{\Delta\nu_{\text{norm.}}}{4.70 \times 10^{-5}}.$$

Photographs were taken of the Zeeman phenomena, using a field strength which varied from 20,000 gauss to a maximum of 32,000 gauss.

Purvis,* in his paper to which reference has been made, gives the strength of the field used in his investigation as 39,000 gauss. This is undoubtedly an over-estimate. A new calculation of his field based on the separation shown by the palladium lines $\lambda 3958.77$ indicates a value of approximately 29,000 gauss. It should also be noted that Purvis gives the lines 3571.30 as unaffected by the magnetic field. This is not in agreement with the present determination. A photograph of the Zeeman resolution shown by this line is reproduced on Plate 8. It is a triplet of type (0)·50.

Most of the Zeeman resolutions for palladium exhibit marked dissymmetries. These dissymmetries have been indicated in the table in the case of those patterns having a central component, by placing the measurement corresponding to the short and long wave-length components to the left and right respectively of the central or zero component. In the case of the lines $\lambda 3258.90$ and $\lambda 3832.41$ the dissymmetries are clearly shown in the photographs reproduced on Plate 8.

Regularities in the Spectrum of Palladium.

The existence of constant difference relations in the spectrum of palladium was first pointed out by Kayser,† who found several triplets with separations 1191 and 3967. Kayser's work was extended by Paulson,‡ who was able to include most of the strong arc lines of palladium. Paulson showed that the difference 3967 was really the sum of two differences, 1628 and 2339. He also called attention to the difference 7755, which occurs three times in the spectrum of palladium.

While the work of Kayser and Paulson points to a very definite regularity which exists between the arc lines of palladium, the exact type of the regularity is not immediately indicated by the numerical relations. The differences are large and an inspection of photographs is of little help in distinguishing separate multiplets. A study of their magnetic resolutions has, however, suggested an arrangement of the arc lines of palladium into a system containing singlet and triplet terms. An analysis has been made in which term combinations have been assigned to practically all the strong lines which occur over the observed range of the arc spectrum. While some of the combinations are believed to

* Purvis, *loc. cit.*

† "Die Spectren der Elemente die Platingruppe," 'Abh. d. Berl. Akad.,' 1897; 'Astrophys J.,' vol. 7, 1899.

‡ Paulson, 'Phil. Mag.,' vol. 29, Jan., 1915.

be established with sufficient certainty, the analysis can scarcely be considered completely satisfactory owing to the non-appearance of certain lines which would be expected to appear with considerable intensity. The multiplicity of the terms, however, is believed to be definitely established, and it is thus possible to make a spectroscopic classification of palladium with respect to the other elements in the periodic table.

The suggested regularities are indicated in Table II. The notation adopted is that of Fowler's *Report on Series in Line Spectra*, triplet terms being indicated by small letters and singlets by capitals. The inner quantum numbers are affixed as subscripts to the letters which represent the terms.

Table II.

		S_0	d_3	d_2	d_1	D_2
	$\Delta\nu$	7754.8	1190.8	2339.0	1627.8	
p_3			27503.8 (10)	26312.9 (6)	23974.1 (3)	22346.3 (3)
p_1	2111.6					
		36179.4 (5)		28424.6 (8)	26085.7 (5)	24457.9 (4)
p_0	1907.4				27993.1 (6)	
D'_2			30410.6 (3)	29219.8 (7)	26880.9 (5)	25253.3 (6)
af_4			(			
			28886.1 (7)	27695.3 (10)		23728.8 (5)
af_3	3360.4					
af_2			(32246.6)	31055.9 (2)	28716.7 (8)	27089.1 (6)
bf_4			29362.8 (10)			
bf_3	3930.4					
			33293.0 (4)	32102.2 (6)		28135.4 (8)
bf_2			(	(	(	(
d'_3	3377.6		30828.5 (9)	29637.6 (6)		25671.0 (6)
d'_2	4972.0		34206.1 (3)	33015.4 (4)	30676.4 (4)	29048.4 (8)
d'_1				37987.3 (0)	(35648.3)	34020.6 (0)
aP_1		40367.7 (3)		32612.8 (5)	30273.7 (6)	28645.9 (6)
bP_1	470.0	40837.7 (3)		33082.8 (5)	30743.8 (4)	29115.9 (6)

In the upper horizontal column of Table II are found the constant wave-number differences which occur most frequently in the spectrum of palladium. A consideration of these constant difference relations in connection with the Zeeman phenomena and the inner quantum selection rules has indicated the existence in the palladium atom of three principal energy levels, represented by singlet and triplet terms. The levels grouped together in this way are a singlet S

level, a triplet d level, and a singlet D. The singlet D term has the same inner quantum number as the triplet d_2 and takes part in similar combinations throughout. The singlet S term with inner quantum number 0 can take part in only a very limited number of combinations.

Of the subordinate levels which combine with the principal levels to which reference has just been made, a triplet p level may be first dealt with. This level combines with the triplet d level, forming the complete multiplet shown in Table II. The Zeeman resolutions give confirmation of this arrangement, and some of them are reproduced as photographs on Plate 8. The line $\lambda 3571\cdot30$, $\nu 27993\cdot1$, was not accounted for in Paulson's system of constant differences. The reason for this is obvious. The term p_0 apparently does not take part in any other combinations and the difference $p_0 - p_1$ does not occur again. The difference $p_1 - p_2$ does occur again when the triplet p level combines with the singlet D. The combination p_0D_2 is forbidden by the inner quantum restrictions, but the combinations of p_1D_2 and p_2D_2 occur and give Zeeman resolutions which are consistent with this arrangement. Only one p term, p_1 , can combine with the singlet S term, and this combination appears in the line $\lambda 2763\cdot29$, $\nu 36179\cdot4$. The Zeeman resolution for this line shows a considerable variation from the predicted separation, but this variation has not seemed great enough to justify discarding the S term.

After the pD and pd combinations had established the existence of the triplet d and singlet D terms, another set of combinations was discovered, believed to be due to a singlet D' term. The D' term with inner quantum number 2 combined with all three members of the triplet d level and with the singlet D in accordance with the inner quantum selection rules. The confirmation given by the Zeeman phenomena for these combinations is regarded as excellent. Some of the photographs are reproduced on Plate 8.

The next two levels indicated in Table II are probably f levels. The evidence for their existence and the grouping suggested are not conclusive, as the multiplets are incomplete. The absence of the combination af_4d_3 is the most serious discrepancy, as it should appear with greater intensity than the other members of the group. The lines of these two groups show the separations $1190\cdot8$, $2339\cdot0$, $1627\cdot8$, which indicate combinations with the triplet d and singlet D terms. The Zeeman effects observed for these lines suggest the fd and fD combinations. In fact, the Zeeman resolutions appear to rule out other possible combinations. The inner quantum selection rules may be considered as not inconsistent with the non-appearance of some of the weaker combinations, but the absence of the strong line f_4d_3 is unexplained.

The next group is believed to be due to a triplet d' level. Very good Zeeman patterns have been secured for some of the members of this multiplet, and the measurements serve to confirm this assignment of terms. The inclusion of the two faint lines $\lambda 2938\cdot55$, $\nu 34020\cdot6$ and $\lambda 2631\cdot69$, $\nu 37987\cdot3$, is based on the constant difference $D_2-d_2 = 3966\cdot7$. Zeeman effects have not been observed for these lines, and it is possible that the relation is accidental. The wave number $\nu 35648\cdot3$ corresponding to the combination d'_1d_1 has been calculated. Regarding the Zeeman pattern of the combination line d'_2D_2 resolution ($0\cdot17$, $0\cdot33$), $0\cdot83$, $1\cdot00$, $1\cdot17$, $1\cdot33$, it must be stated that with the resolution obtained it does not show the expected absence of the central component, as does the corresponding combination D'_2d_2 .

The remaining lines in Table II are accounted for by the introduction of two singlet P terms. The inner quantum selection rules are obeyed in the combinations of these terms with the triplet d terms and with the singlet D and singlet S terms. The Zeeman effects, on the other hand, are only confirmatory in so far as the general form of the patterns is concerned. The actual measurements show large variations from the resolutions calculated for these combinations. The combinations indicated require a term having an azimuthal quantum number 2 and an inner quantum number 1. The only term beside the singlet P which satisfies these conditions is the triplet term p_1 . The Zeeman effects given by the combination of this term with a triplet d level are well known and easily recognized. They serve to eliminate this possibility and to make it seem more probable that the singlet P terms are correct.

An examination of the constant difference relations in Table II shows that the ratio of the separations of terms in the main triplet d level is reversed, the difference d_1-d_2 being larger than the difference d_2-d_3 . If the suggested combinations d'_1d_2 and d'_1D_2 given in Table II are correct, the ratio of separations in the d' level is also reversed. A similar behaviour of the separation ratio has been observed for the d term in the first diffuse triplet of mercury.* A similar case is also found in the arc spectrum of iron, where Walters† and Laporte‡ have found a quintet p level in which the separation ratio is reversed.

The spectrum of palladium presents an interesting analogy with that of mercury in the manner in which the triplet d and singlet D terms are closely associated, in their combinations with other terms. The spectrum of mercury

* A. Fowler, 'Report on Series in Line Spectra' (Fleetway Press, London, 1922).

† Walters, *loc. cit.*

‡ Laporte, *loc. cit.*

exhibits an inter-combination series $1p - mD$ which runs parallel to the diffuse triplet series $1p - md$, and another inter-combination series $1P - md$ which is parallel to the corresponding series of singlets.

As indicated before, Table I contains a list of wave-lengths and wave numbers of palladium lines, with the term combinations and observed and calculated Zeeman effect for each line. The information given by the Zeeman phenomena is presented in more compact form in Table III. Table III is of the same form as Table II, except that in place of the wave-numbers and intensities of the lines there are placed the calculated and observed Zeeman patterns for the various combinations. In each case the theoretical resolution is placed above and the actual measurements directly below it.

For the spectra of those elements which do not form characteristic series, it is not, in general, possible to assign definite values to the terms. It is possible, however, to assign an arbitrary value to one of the terms, and when this is done the relative values of the other terms may be readily calculated.

A knowledge of the relative values of the terms throws light on the arrangement of energy levels in the atom and facilitates the calculation of additional combinations. The relative term values for palladium are found in Table IV. An arbitrary value of 60,000 has been assigned to the term d'_1 and the other terms have been calculated from it. Table IV also contains a list of the combinations which have been discovered. An examination of the Table shows that any additional combinations which might be expected, such as $d' - p$, would be in the infra-red and so would not come within the range of the present investigation.

Zeeman Effect for other Elements.

As stated previously, photographs have been taken of the Zeeman effect of nickel. Two of these photographs, reproduced on Plate 8, show the resolutions given by the nickel lines $\lambda 3597.84$ and $\lambda 3722.63$, corresponding to the combinations p_1d_1 and p_2d_1 respectively. In the photograph reproduced of the latter combination, the components are not completely resolved, but an analysis of the pattern which has been made with a nicol prism leaves little doubt that this line has been correctly identified. The separations of the Zeeman components observed for these lines are as follows:— $\lambda 3597.84$, resolution (0.87) 0.48, 1.49; $\lambda 3722.63$, resolution (0.0, 0.94) 1.56, 2.56. The corresponding patterns for palladium lines are reproduced on Plate 8.

Plate 8 also contains photographs of the calcium doublet $\lambda 3933.66$, $\lambda 3968.46$, the silver doublet $\lambda 3280.66$, $\lambda 3382.86$, and the iron line $\lambda 3722.56$, which is one of the lines identified by Laporte¹ as belonging to a d_2f_2 com-

Table III.

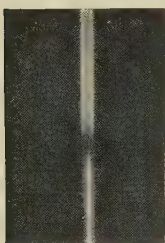
382

C. S. Beals.

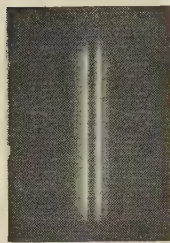
	S_0	d_3	d_2	d_1	D_2
p_2		(0·0, 0·17, 0·34), 1·00, 1·17, 1·33, 1·50, 1·67 (0), 1·27	(0·33, 0·67), 0·83, 1·17, 1·50, 1·83 (0·40, 0·70), 1·11, 1·43, 1·86	(0·0, 1·00), 0·50, 1·50, 2·50 (0·0, 0·97), 1·50, 2·49	(0·50, 1·00), 0·50, 1·00, 1·50, 2·00 0·44, 0·93, 1·32, 1·79
p_1	(0) 1·50 (0) 1·30		(0·0, 0·33), 0·83, 1·17, 1·50 (0), 0·16	(1·00), 0·50, 1·50 (0·91), 0·50, 1·43 (0), 0·50 (0), 0·52	(0·0, 0·50), 0·50, 1·00, 1·50 (0·0, 0·40), 0·95
p_0					
D'_2		(0·0, 0·33, 0·67), 0·67, 1·00, 1·33, 1·67, 2·00 (0), 1·74	(0·17, 0·33), 0·83, 1·00, 1·17, 1·33 (0·33), 1·11	(0·0, 0·50), 0·50, 1·00, 1·50 0·0, 0·49, 1·01, 1·49	(0), 1·00 (0), 1·00
f_3		(0·25, 0·50, 0·75), 0·58, 0·83, 1·08, 1·33, 1·58, 1·83 (0·72), 1·39	(0·0, 0·08, 0·17), 0·92, 1·00, 1·08, 1·17, 1·25 (0), 1·05		(0·0, 0·08, 0·17), 0·92, 1·00, 1·08, 1·17, 1·25 (0), 1·09
f_2		(0·0, 0·67, 1·33), 0·67, 1·33, 2·00, 2·67	(0·50, 1·00), 0·17, 0·67, 1·17, 1·67 0·69	(0·0, 0·17), 0·50, 0·67, 0·83 (0), 0·99	(0·33, 0·67), 0·33, 0·67, 1·00, 1·33 (0·55), 0·55, 1·00, 1·40
f_4		(0·0, 0·08, 0·17, 0·25), 1·00, 1·08, 1·17, 1·25, 1·33, 1·42, 1·50 (0), 1·16			
f_3		(0·25, 0·50, 0·75), 0·58, 0·83, 1·08, 1·33, 1·58, 1·83 0·69	(0·0, 0·08, 0·17), 0·92, 1·00, 1·08, 1·17, 1·25 (0), 1·02		(0·0, 0·08, 0·17), 0·92, 1·00, 1·08, 1·17, 1·25 (0), 1·17
d'_3		(0), 1·33 (0), 1·36	(0·0, 0·17, 0·33), 1·00, 1·17, 1·33, 1·50, 1·83 (0), 1·51		(0·0, 0·33, 0·67), 0·67, 1·00, 1·33, 1·67, 2·00 (0), 1·65
d'_2		(0·0, 0·17, 0·33), 1·00, 1·17, 1·33, 1·50, 1·83 (0), 1·44	(0), 1·17 (0), 1·16	(0·0, 0·67), 0·50, 1·17, 1·83 0·0, 0·63, 1·16, 1·84 (0), 0·50	(0·17, 0·33), 0·83, 1·00, 1·17, 1·33 (0), 1·09
d'_1			(0·0, 0·67), 0·50, 1·17, 1·83		(0·0, 0·50), 0·50, 1·00, 1·50
aP_1	(0), 1·00 —		(0·0, 0·17), 1·00, 1·17, 1·33 (0), 1·34	(0·50), 0·50, 1·00 (0·36), 0·38, 0·85	(0), 1·00 (0), 1·23
bP_1	(0), 1·00 —		(0·0, 0·17), 1·00, 1·17, 1·33	(0·50), 0·50, 1·00 (0·32), 0·59	(0), 1·00 (0), 1·31



a, b, Pd arc, Fe comparison. Fourth order grating.
c. Pd arc. Quartz Littrow spectrograph.

PD $\lambda 3571\cdot30$ 

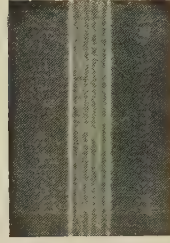
$p_0 d_1$
(0) 50

PD $\lambda 3799\cdot33$ 

$p_2 d_2$
(33, 67) 83, 117
150, 183

PD $\lambda 3832\cdot41$ 

$p_1 d_1$
(100) 50, 150

PD $\lambda 4170\cdot00$ 

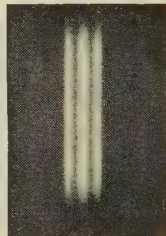
$p_2 d_1$
(0, 100) 50, 150,
250

PD $\lambda 3958\cdot77$ 

$D'_2 D_2$
(0) 100

PD $\lambda 3719\cdot06$ 

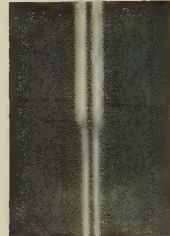
$D'_2 d_1$
(0, 50) 50, 100,
150

PD $\lambda 3894\cdot33$ 

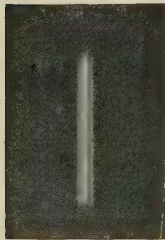
$d'_3 D_2$
(0, 33, 67) 67, 100,
133, 167, 200

PD $\lambda 3302\cdot25$ 

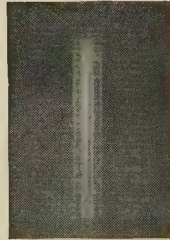
$P_1 d_1$
(50) 50, 100

PD $\lambda 3690\cdot49$ 

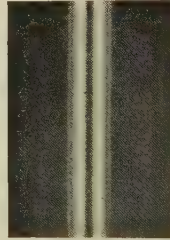
$f_2 D_2$
(33, 67) 33, 67,
100, 133

PD $\lambda 3421\cdot36$ 

$D'_2 d_2$
(17, 33) 83, 100,
117, 133

PD $\lambda 3258\cdot90$ 

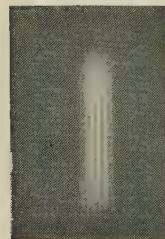
$d'_2 d_1$
(0, 67) 50, 117, 183

FE $\lambda 3722\cdot56$ 

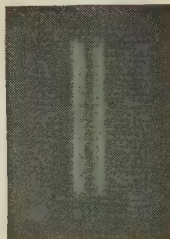
$^5f_2 ^5d_2$
(50, 100) 50, 100
150, 200

NI $\lambda 3597\cdot84$ 

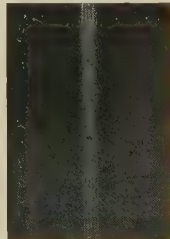
$p_1 d_1$
(100) 50, 150

CA $\lambda 3933\cdot66$ 

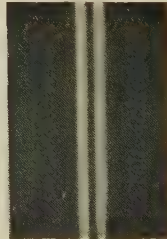
$\sigma_1 \pi_2$
(33) 100, 166

CA $\lambda 3968\cdot46$ 

$\sigma_1 \pi_1$
(66) 133

AG $\lambda 3280\cdot66$ 

$\sigma_1 \pi_2$
(33) 100, 166

AG $\lambda 3382\cdot86$ 

$\sigma_1 \pi_1$
(66) 133

NI $\lambda 3722\cdot63$ 

$p_2 d_1$
(0, 100) 50, 150,
250

Table IV.—List of Combinations and Term Values.

Combinations.	Relative terms.		
$p - S$		$bP_1 = 55095.4$	
$p - d$			
$p - D$		$aP_1 = 54625.4$	
$D' - d$			
$D' - D$	{	$d'_1 = 60000.0$	$\Delta d_{12} = 4972.0$
$af - d$		$d'_2 = 55028.0$	
$af - D$		$d'_3 = 51650.4$	
$bf - d$		$\Delta d_{23} = 3377.6$	
$bf - D$			
$d' - d$			
$d' - D$	{	$bf_2 = \text{---}$	$\Delta f_{34} = 3930.0$
$aP - S$		$bf_3 = 54114.9$	
$aP - d$		$bf_4 = 50184.5$	
$aP - D$			
$bP - S$	{	$af_2 = 53068.6$	$\Delta f_{23} = 3360.5$
$bP - d$		$af_3 = 49708.1$	
$bP - D$		$af_4 = \text{---}$	
		$D'_2 = 51232.6$	
	{	$p_0 = 52344.8$	$\Delta p_{01} = 1907.4$
		$p_1 = 50437.4$	
		$p_2 = 48325.7$	
		$D_2 = 25979.5$	
	{	$d_1 = 24351.7$	$\Delta d_{12} = 2339.0$
		$d_2 = 22012.7$	
		$d_3 = 20821.9$	
		$S_0 = 14257.9$	$\Delta d_{23} = 1190.8$

bination in a quintet system. All of these lines appeared as impurities in the palladium spectrum, and they serve to illustrate the method of securing sharp Zeeman patterns for reversed lines by observing them as impurity lines in the spectra of other substances. The calcium lines appeared as impurities in the palladium spark, while the lines of silver and iron are reproduced from photographs of arc spectra.

Summary of Results.

New measurements have been made of the Zeeman effect for palladium. Measurements are recorded for some patterns not previously observed, and more

complete resolution has been obtained for some lines previously observed with inadequate resolving power.

An analysis of the palladium spectrum on the basis of its Zeeman phenomena has indicated that the arc lines consist of singlets, triplets, and inter-combinations between singlet and triplet terms.

The discovery of odd multiplicities in the spectrum of palladium confirms the expected divisions in the eighth group of the periodic table, and suggests a re-arrangement into three sub-groups corresponding to the three vertical columns.

In concluding this paper the writer wishes to express his appreciation of the kindness of Prof. A. Fowler, F.R.S., who suggested the investigation and who has generously given assistance and advice during the progress of the work.

A Determination of the Variation of the Mass of the Electron with Velocity, using Homogeneous β -Rays.—Preliminary Results.

By R. A. R. TRICKER, B.A., Trinity College, Cambridge.

(Communicated by Prof. Sir Ernest Rutherford, F.R.S.—Received July 7, 1925.)

[PLATE 9.]

Since the pioneer experiments of Kaufmann many investigations have been made to test the variation of the mass of the electron with velocity, with the object of distinguishing between the classical and relativistic mechanics. However, the number of distinct methods employed is not large, and they may be divided into two classes, according to whether cathode rays from a discharge tube, or the faster natural β -radiation from the radio-active substances were used.

Of the experiments with cathode rays, few have reached the very high degree of precision necessary, since the velocity of the electrons in this case is comparatively small (up to a half that of light), and the various theories approximate to each other. In more recent years the accuracy has been increased considerably by the special methods employed by Guye in collabora-

tion with Lavanchy and Ratnowsky,* and their results form a confirmation of the theory of relativity.

The well-known experiments of Bucherer† (repeated by Neumann‡) using a radio-active substance as the source of electrons, are the only accurate investigations at higher velocities. The β -rays employed in these experiments, being derived from a comparatively thick layer of radio-active material, possess a continuous distribution of velocities, and homogeneous beams were selected by the combined action of the magnetic field and an electric field between two parallel plates, very close together, forming a condenser. However, this selection is not quite complete, and the lack of homogeneity in the rays emerging from the condenser, sets a limit to the accuracy of the experiment, and in particular makes the application of the method to very high velocities difficult.§ This is not easily corrected theoretically, as even with the plates of the condenser infinitely close together there will always be a certain ambiguity due to the reflection of the rays from their surfaces. If this lack of homogeneity be neglected, the photographs obtained by Bucherer diverge widely from the theoretical at high velocities.

When the source of radiation consists of a very thin deposit of radio-active matter, it is well known that the β -rays are of two kinds—one, a number of groups of particles with definite velocities (the lines of the magnetic spectrum) arising from the conversion of γ -rays in the various atomic levels, and the other, electrons with a continuous range of velocities (forming the background of the spectrum). The lines of definite velocity have recently received much careful study at the hands of several investigators, the momenta of the electrons (as measured by the radius of curvature of their path in a magnetic field) from radium B and C in particular having been measured very accurately (to 1 in 500) by Ellis and Skinner.|| These lines furnish a ready-made source of rays of great homogeneity, and experiments could be made on them which would obviate almost completely the difficulty met with in Bucherer's arrangement, mentioned above. Experiments on these lines are described in the following paper.

The method employed consisted in sending the β -rays through, first an accelerating and then a retarding electric field, in a special focussing apparatus,

* Guye, Ratnowsky et Lavanchy, 'Mém. de la Soc. de Phys. de Genève,' vol. 39, f. 6 (1921).

† 'Ann. d. Phys.,' vol. 28, p. 974 (1909).

‡ 'Ann. d. Phys.,' vol. 45 (1914).

§ Cf. Lewis, 'Roy. Soc. Proc.' (March, 1925).

|| Ellis and Skinner, 'Roy. Soc. Proc.,' A, vol. 105 (1924).

and measuring the distance between the traces on the plate so formed. As yet, however, the deflections obtained by reversing the electric field are on the small side, with the potential difference available, being from 5 mm. to 4 cm. It is hoped to repeat these measurements shortly with a higher voltage, which should increase the accuracy some four times. At present the method gives the same order of precision as that obtained by Bucherer, and seems less open to objection than the arrangement used by that author.

Owing to the axial symmetry, the helical method of focusing the rays due to Dr. Kapitza and described before,* is more suitable than the ordinary apparatus.† A source of radiation is placed in a magnetic field, and rays fired at a certain angle α to the lines of force are selected by means of an annular slit. These rays are brought to a focus on a film suspended on the axis of the slit on the side remote from the source. In the following experiments little alteration was made in the arrangement, the electric field being applied parallel to the axis of the apparatus, between a brass plate, to which the source is attached, and a piece of gauze held parallel to the plate and distant 5 mm. from it. Thus it is possible to measure directly the change in $(H\rho)$ produced by the field. Since between the source and the gauze the electric and magnetic fields act simultaneously, the theory becomes rather more complicated than would be the case if the electric field could be applied first and the resulting value of $(H\rho)$ measured afterwards in a magnetic field.

The trajectory is divided into two parts, the first being where the rays are under the influence of the electric and magnetic fields, parallel to the axis of the apparatus, and the second outside the electric field, where the magnetic field acts alone. Taking the axis of x parallel to the fields, on the theory of relativity the equations of motion within the electric field are

$$\frac{d}{dt} \left\{ \frac{m_0 \dot{x}}{\left(1 - \frac{q^2}{c^2}\right)^{\frac{1}{2}}} \right\} = Ee; \quad (1)$$

$$\frac{d}{dt} \left\{ \frac{m_0 \dot{y}}{\left(1 - \frac{q^2}{c^2}\right)^{\frac{1}{2}}} \right\} = He\dot{z}; \quad (2)$$

$$\frac{d}{dt} \left\{ \frac{m_0 \dot{z}}{\left(1 - \frac{q^2}{c^2}\right)^{\frac{1}{2}}} \right\} = -He\dot{y}; \quad (3)$$

$$q^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2, \quad (4)$$

where the letters have their usual significance.

* 'Proc. Camb. Phil. Soc.,' vol. 22, pt. 3.

† Used by Rutherford, Robinson and Rawlinson, Ellis and others.

Outside the electric field, the right-hand side of 1 is zero. These equations may be solved, and the distance from the source at which the rays re-cross the axis (*i.e.*, the position of the photographic trace) found. The solution being a somewhat cumbersome process, the following approximation is sufficient to illustrate the calculations.

The potential difference in the electric field is always small (5,000 volts) compared with the "energy" of the rays initially (500,000 volts), and thus, to a first approximation, the mass will remain constant throughout (corresponding to its practically constant velocity), and the equations reduce to*

$$m\dot{x} = Ee; \quad (1A)$$

$$m\dot{y} = He\dot{z}; \quad (2A)$$

$$m\ddot{z} = -He\dot{y}; \quad (3A)$$

$$m = \frac{m_0}{(1 - v^2/c^2)^{\frac{1}{2}}}. \quad (4A)$$

The equations (2A) and (3A) are not affected by the electric field, and hence

$$y = \frac{mv}{eH} \sin \frac{eH}{m} t; \quad (5A)$$

$$z = \frac{mv}{eH} \left[\cos \left(\frac{eH}{m} t \right) - 1 \right], \quad (6A)$$

where

$$v^2 = \dot{y}^2 + \dot{z}^2.$$

The motion projected on the yz plane is circular, and the particles still re-cross the axis at a time

$$t = 2\pi \sqrt{\frac{eH}{m}}. \quad (7A)$$

If t' is the time taken to reach the edge of the electric field, which is in the plane $x = h$,

$$t' = \frac{-u \pm \sqrt{u^2 + 2heE/m}}{eE/m}. \quad (8A)$$

The terminal value of $\dot{x}$ on leaving the electric field is

$$\dot{x}' = \sqrt{u^2 + 2heE/m}. \quad (9A)$$

Also, the time taken by the particles to go from the end of the electric field to the point at which they re-cross the axis is

$$t'' = \frac{2\pi m}{eH} - t',$$

* This should be true for lines of low velocity.

and hence the distance from the end of the electric field to the trace on the film is

$$l = \sqrt{(u^2 + 2heE/m)} \left[\frac{2\pi m}{eH} - \frac{\sqrt{(u^2 + 2heE/m)} - u}{eE/m} \right],$$

and the total distance from the source is

$$R = h + l.$$

Now, these calculations will hold only as far as the first order in hE/mu^2 ; consequently, approximating the value of l to this order, the following expression is obtained for R :—

$$R = R_0 + (R_0 - \frac{1}{2}h) \cdot \frac{heE}{mu^2}, \quad (10A)$$

where $R_0 = 2\pi um/eH$ and is the range the particles would have in the magnetic field alone, if they started with the initial velocities u, v, w .

A more complete calculation, using equations (1), (2) and (3) instead of (1A), (2A), and (3A), gives the following expression for the range R :—

$$R = h + c \left\{ \frac{E^2 e^2 h^2}{c^2} + \frac{2Eehm_0}{(1 - q_0^2/c^2)^{\frac{3}{2}}} + \frac{m_0^2 u^2}{(1 - v^2/c^2)} \right\}^{\frac{1}{2}} \\ \left[\frac{2\pi}{Hec} - \frac{1}{Ee} \log_e \left\{ \frac{\frac{Eeh}{c} + \frac{m_0 c}{(1 - q_0^2/c^2)^{\frac{3}{2}}} + \left[\frac{E^2 e^2 h^2}{c^2} + \frac{2Eehm_0}{(1 - q_0^2/c^2)^{\frac{3}{2}}} + \frac{m_0^2 u^2}{1 - v^2/c^2} \right]^{\frac{1}{2}}}{\frac{m_0 c}{(1 - q_0^2/c^2)^{\frac{3}{2}}} + \frac{m_0 c}{(1 - q_0^2/c^2)^{\frac{3}{2}}}} \right\} \right].$$

This may be expanded as before in ascending powers of E and gives the following expression for the range of the particles:—

$$R = R_0 + (R_0 - \frac{1}{2}h) \frac{\left(1 - \frac{q_0^2}{c^2}\right)^{\frac{3}{2}}}{m_0 u^2} \cdot Eeh \\ - \left[R_0 \left(1 - \frac{u^2}{c^2}\right) - h \left(1 - \frac{2u^2}{3c^2}\right) \right] \cdot \frac{\left(1 - \frac{q_0^2}{c^2}\right)}{2m_0^2 u^4} E^2 e^2 h^2 \\ + \left[R_0 \left(1 - \frac{u^2}{c^2}\right) - \frac{5h}{4} \left(1 + \frac{11u^2}{15c^2}\right) \right] \frac{\left(1 - \frac{q_0^2}{c^2}\right)}{2m_0^3 u^6} E^3 e^3 h^3 \\ - \dots \quad (6)$$

Owing to the fact that in the experiments the field E is reversed, and the doubled deflection measured, the term in E^2 being always of the same sign does not affect the magnitude of the displacement. However, it enters into the

estimation of R_0 from the traces, as it makes the accelerated and retarded deflections unequal in magnitude. The term in E^3 is only of importance in the case of the lines of lowest energy, and then only to the extent of 1 per cent.

Before the theory can be compared with the experimental results, it is necessary to enquire into the significance of the quantity denoted by R_0 above. In equation (10A) R_0 was defined as $2\pi mu/eH$, and is the range a particle would have if projected in the absence of an electric field, with a velocity whose components are u, v, w with which the particle actually started in the field. In general, owing to the curving of the track by the electric field, u, v, w are not the components of the velocity possessed by the system of particles selected by the slit in the absence of the field. When the rays are accelerated by the field, the angle α which the initial part of the trajectory makes with the axis will be greater than the normal, as indicated (fig. 1), and thus R_0 will be less than R_{00} —the range of the particles selected by the slit without the electric field. In the same way when the particles are retarded, the angle α will be decreased, so that R_0 will be greater than R_{00} .

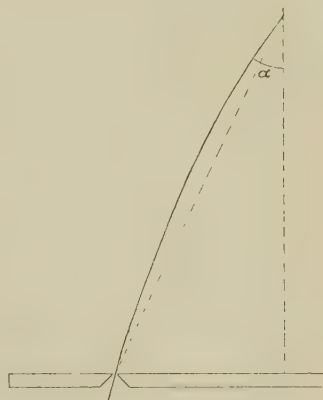


FIG. 1.

Thus, when accelerated the range R_0 (fig. 2) will be represented on the film by some point R_{01} , nearer the source than R_{00} , and the deflection will be given

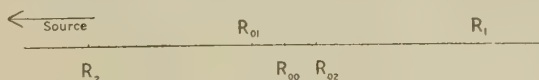


FIG. 2.

by $R_{01}R_1$. In the same way when retarded R_0 will be represented by some point R_{02} , and the observed displacement R_1R_2 will be less than $2(R - R_0)$ as given by 6, by $R_{01}R_{02}$. A calculation to the same approximation as that used above will be made to determine $R_{01}R_{02}$.

If r is the radius of the slit used in the apparatus, squaring and adding (5A) and (6A) gives

$$r^2 = y^2 + z^2,$$

and therefore

$$r = \frac{2vm}{eH} \sin \cdot \frac{eHt}{2m}.$$

If h' is the distance of the source from the slit, equations 8A and 9A give, for the time taken by the rays to reach the slit from the source,

$$t = \frac{-u + (u^2 + 2heE/m)^{\frac{1}{2}}}{eE/m} + \frac{h' - h}{(u^2 + 2heE/m)^{\frac{1}{2}}}.$$

Expanding this to the first order in E this reduces to

$$t = \frac{h'}{u} - (h' - \frac{1}{2}h) \frac{heE}{mu^3},$$

and, substituting in the expression for r ,

$$r = \frac{2vm}{eH} \sin \left\{ \frac{eH}{2m} \left[\frac{h'}{u} - (h' - \frac{1}{2}h) \frac{heE}{mu^3} \right] \right\},$$

or

$$\frac{\pi r}{R_0 \tan \alpha} = \sin \frac{\pi}{R_0} \left\{ h' - (h' - \frac{1}{2}h) \frac{heE}{mu^2} \right\}.$$

This gives the connection between the initial constants u , v , w , or $\tan \alpha$, and Eh in terms of the radius r of the slit. Writing $R_{00} + dR_{00}$ for R_0 , $\alpha + d\alpha$ for α , and dropping the suffixes for convenience, the above reduces to

$$\begin{aligned} \frac{\pi r}{R \tan \alpha} - \frac{\pi r dR}{R^2 \tan \alpha} - \frac{\pi r}{R} \operatorname{cosec}^2 \alpha d\alpha \\ = \sin \left[\frac{\pi}{R} \left\{ h' - \frac{h' dR}{R} - (h' - \frac{1}{2}h) \frac{heE}{mu^2} \right\} \right] \\ = \sin \frac{\pi h'}{R} - \frac{\pi}{R} \left\{ \frac{h' dR}{R} + (h' - \frac{1}{2}h) \frac{heE}{mu^2} \right\} \cos \frac{\pi h'}{R} \end{aligned}$$

to the first order in small quantities.

But

$$\frac{\pi r}{R \tan \alpha} = \sin \frac{\pi h'}{R}; \quad \frac{dR}{R} = -\tan \alpha d\alpha.$$

Hence

$$\frac{dR_{00}}{R_{00}} = (h' - \frac{1}{2}h) \frac{heE}{mu^2} \cdot \frac{\cos \frac{\pi h'}{R}}{\left(r \cot^3 \alpha + h' \cdot \cos \frac{\pi h'}{R} \right)} \quad (7)$$

Thus, summarising the results of the whole theory given above, it is found that the deflection D which is observed is given (as far as the first order in E) by,

$$\begin{aligned} D = (R_0 - \frac{1}{2}h) \frac{(1 - q_0^2/c^2)^{\frac{1}{2}}}{m_0 q_0^2 \cos^2 \alpha} heE \\ - (h' - \frac{1}{2}h) \cdot \frac{heE}{m_0 q_0^2 \cos^2 \alpha} \frac{(1 - q_0^2/c^2)^{\frac{1}{2}} \cos \frac{\pi h'}{R}}{\left(r \cot^3 \alpha + h' \cos \frac{\pi h'}{R} \right)}, \quad (8) \end{aligned}$$

the angle α being obtained from the radius of the slit and the range from the formula

$$\tan \alpha = \frac{\pi r}{R \sin \frac{\pi h'}{R}}. \quad (9)$$

The above discussion shows how to calculate the deflections that would be expected on the theory of relativity. For purposes of comparison it is useful to have the corresponding values on Abraham's theory of the rigid electron. Expressed as a series in ascending powers of q/c , the expressions for the mass of the electron on this theory are very similar to those obtained on the theory of relativity. Hence, from reasons similar to those used to justify the approximate theory given above, namely, that the change in velocity of the particles produced by the fields is small, it is to be expected that formulæ (6) and (7) will hold, on Abraham's theory, to the first order in E , if the appropriate substitution be made for the mass. To facilitate calculation, curves were drawn showing mq/e and mq^2/e , deduced on the theory of the rigid electron, as functions of the velocity q , and these enable q to be obtained on this theory from both the value of $(H\rho)$ obtained magnetically, and from the deflections obtained, which are proportional to mq^2/e .

Accurate measurements of the quantity $(H\rho)$ for the β -ray lines have been made by Ellis and Skinner,* whose results are probably correct to 1 in 500, this quantity being deduced directly from observations of the radius ρ of the path of the rays in a magnetic field, and is thus independent of all theories of the constitution of the electron. The method adopted for comparing the experimental results with the theory is to compare the value deduced for the velocity q from the deflections in the electric field with that obtained from $(H\rho)$.

Apparatus.—The apparatus is essentially the same as that employed before, and is represented in the diagram, fig. 3.

At the top on the axis of the annular slit C, the source A is held by means of a brass plate B, which forms one terminal of the electric field. An emanation tube was tried for a source, but was not found to give sufficiently satisfactory results, and its use was abandoned. It was replaced by the radioactive deposit from radium emanation, on a piece of platinum foil 5 mm. by 3 mm., placed with the shorter side of the rectangle parallel to the axis of the instrument and with the plane of the foil parallel to the film E. This arrangement gives the cross-shaped trace, which, as mentioned before, is the form best

* *Loc. cit.*

adapted for measurement, and also has the advantage that chance fluctuations in the fields (which might possibly be different for the two traces) do not

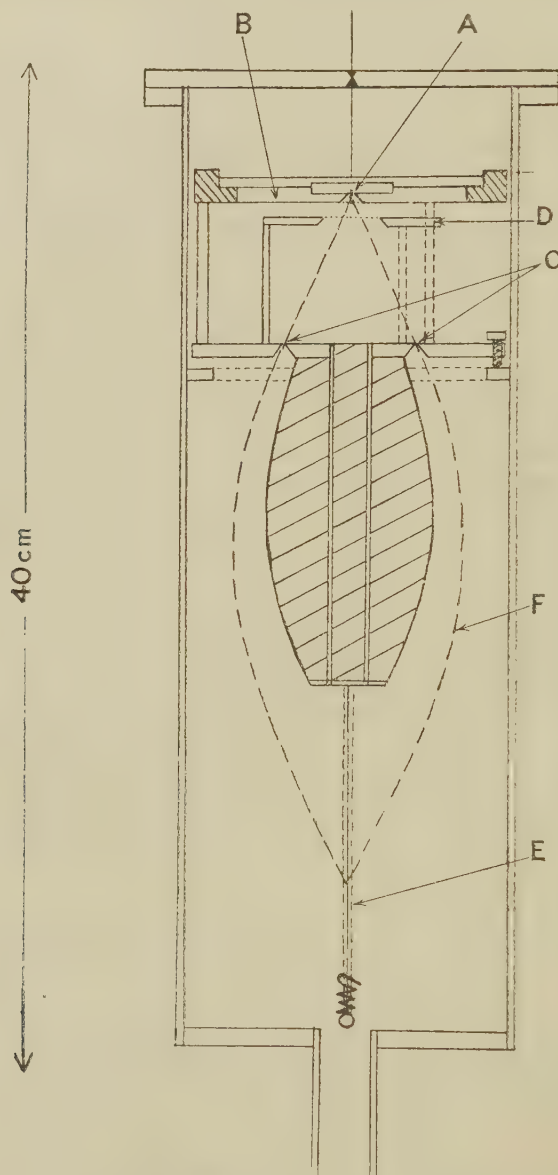


FIG. 3.—A. Source. B. High Tension Plate. C. Slit. D. Earthed Plate. E. Film.
F. Envelope of Trajectories.

displace the point of measurement, as they would the edge of a line, the measurements being made at the centre of the trace.

The source fits into a slot in the brass plate, and is covered with copper gauze, flush with the surface of the plate, so as to obtain as uniform an electric field as possible.

The Electric Field.—The electric field was formed between the plate holding the source, and a second brass plate, D, fig. 3, supported about 5 mm. from the first, and connected through the surrounding brass box to earth. The centre of the plate was removed and the hole covered with gauze, through which the rays passed. The field itself was produced by charging the source and its supporting plate to a potential of 5,000 volts positive or negative, by means of an Evershed motor generator, run at a constant rate.

The field was reversed every three minutes during an exposure by means of a commutator, except in the case of the first five films tabulated, when it was reversed once only, in the middle of the exposure. The latter process is not so accurate as the former, since gradual variations in the fields will affect the displacements, and consequently in arriving at the mean of the observations these films were given half the weight of the others.

The potential difference between the plates was indicated during the experiments by means of an electrostatic voltmeter, which enabled the field to be regulated and kept constant. Since the intensity has to be known directly, the instrument was calibrated several times by means of a potentiometer.

The Magnetic Field.—The whole apparatus was placed inside a solenoid producing the requisite magnetic field. The falling off at the ends of the coil was corrected by means of two smaller coils placed at either end. The uniformity of the magnetic field only enters into the result as a second-order term, and a rough calculation showed that it could be neglected to the degree of accuracy attained in the experiments. This calculation was checked by an application of it to several films taken without the end coils, on which the displacement differed by as much as 5 per cent. from the theoretical value, and it was found to correct these values to the same order of accuracy as that obtained with the more uniform field.

Vacuum.—The apparatus had to be exhausted to a sufficiently high vacuum, to prevent a discharge taking place. It was found possible to commence the exposure when the McLeod gauge, which was used to indicate the pressure, registered $2 \cdot 10^{-4}$ mm. of mercury, although, owing to the grease and other vapours which might not be taken up completely by the liquid-air trap applied, the pressure in the apparatus was probably somewhat higher. The evacuation was performed by a metal diffusion pump, and occupied 20 minutes before the exposure could be started.

The exposure given was usually of the order of one hour, a source of 10 mgm. equivalent activity, initially, requiring about 80 minutes for the two traces (40 minutes each).

The photographs were taken on a strip of double-sided film (indicated by E in fig. 3), cut from a sheet of Eastman's "duplitised X-ray film."

The traces so formed were found to be fairly sharp, and good ones could be measured to a few hundredths of a millimetre. The accompanying Plate 9 shows the type of photograph obtained, the reproduction being enlarged three diameters. The upper spectrum shows the cross-shaped traces due to the lines ($H\rho$) 1410 and ($H\rho$) 1677, the electric field not being applied. That immediately underneath shows the same two lines taken under the action of the electric field. The lower spectrum contains the lines ($H\rho$) 1677 and ($H\rho$) 1938. The films were found to be quite free from fogging by discharge of the electric field, unless, of course, the pressure rose in the apparatus, due to a leak when the darkening was complete and rapid.

Results.—The following tables are derived from measurements on some nine films, the lines on which are sharp and easily seen and which were taken under the standard conditions. As explained before, five of these, however, were photographed with a single reversal of the electric field, and are probably not quite so accurate as those in which the field was reversed many times during the course of an exposure, this being allowed for in arriving at the mean. The results are of a preliminary nature and are not claimed to be final or exhaustive.

From the displacement the value of the velocity q was calculated. Since this quantity enters into the expression for the displacement in the form mq^2 , an error in the measurement of the traces is converted into less than half the error in the velocity—for on the theory of relativity

$$mq^2 \quad : : \quad \frac{q^2}{\left(1 - \frac{q^2}{c^2}\right)^{\frac{3}{2}}},$$

and hence

$$\frac{d[m \cdot q^2]}{m \cdot q^2} = \left(\frac{2}{q} + \frac{q}{c^2 - q^2} \right) dq.$$

At the same time, of course, this method of expressing the result produces a corresponding decrease in the difference between the theories to be compared.

The following table shows the order of accuracy attained up to the present, and consists of the individual readings taken from the four last films. The first column contains the value of ($H\rho$) for the β -ray line concerned, obtained



a. Lines $[H\rho]$ 1410, 1677 without electric field.

b. The same with electric field.

c. Lines $[H\rho]$ 1677, 1938.

Enlarged approx. three diams.

from the experiments of Ellis and Skinner.* The second contains the observed deflections measured in millimetres, which is a mean of ten readings made on each line. From this and the value of R_0 , $(H\rho) q$ was deduced from equation 8, and this was tabulated in the next column. The last two columns contain the value of this quantity obtained theoretically, on the theory of relativity (Einstein), and on that of the rigid electron (Abraham) respectively, from the value of $(H\rho)$.

The value assumed for e/m_0 was $1770 \cdot 10^7$ e.m.u.

Table. (Individual Readings.)

$(H\rho)$.	Deflection.	$(H\rho) \cdot q_{\text{obs.}}$	$(H\rho) \cdot q_{\text{Ein.}}$	$(H\rho) \cdot q_{\text{Ab.}}$
660.9	36.41 mm.	$718 \cdot 7 \cdot 10^{10}$	$716 \cdot 7 \cdot 10^{10}$	$723 \cdot 10^{10}$
1410	8.99	2673	2696	2800
1677	6.65	3525	3528	3685
1938	6.17	4357	4365	4580
2256	4.84	5346	5400	5690

The second table contains the average values obtained from the total of nine films on which the measurements were made. The first column gives, as before, the value of $(H\rho)$ for the line given by Ellis and Skinner. The second is the number of different films on which the line was measured. The third is the mean value of $(H\rho) \cdot q$ obtained as before, and the fourth column is the corresponding value of the velocity, expressed as a fraction of the velocity of light, while the fifth column is the theoretical value of q/c on relativity theory. The sixth and seventh columns contain the quantity corresponding to that in the fourth and fifth, calculated on Abraham's theory.

Table.

$(H\rho)$.	No. of films.	$(H\rho) \cdot q_{\text{obs.}}$	Einstein.		Abraham.	
			$q_{\text{obs.}}$	$q_{\text{calc.}}$	$q_{\text{obs.}}$	$q_{\text{calc.}}$
660.9	2	$719 \cdot 4 \cdot 10^{10}$	0.3630c	0.3615c	0.341c	0.367c
1410	2	2680.7	0.6387	0.6371	0.653	0.665
1677	5	3501	0.7009	0.7014	0.722	0.736
1938	3	4344	0.7511	0.7509	0.776	0.790
2256	1	5346	0.7938	0.7979	0.827	0.843

* *Loc. cit.*

It is seen that the observed deflections agree better with the values given by the theory of relativity than with those given by that of the rigid electron. It was calculated that the maximum error in the observed deflections was about 2 per cent., while the theories differ by about 5 per cent. At the same time the number of readings taken is rather limited. However, it was not thought worth while to increase the number of these at present, as a source of higher potential will be forthcoming in the near future, when the experiments will be repeated, and it is hoped that the accuracy of the measurements will be increased.

Errors.—The errors occurring in the above measurements are partly inherent in the method itself, and partly introduced indirectly from other experiments. Of the former the most important is the uncertainty in the value of the potential applied to the source. Although at any one time the readings of the electrostatic voltmeter could be calibrated more accurately, they varied as much as $\frac{1}{2}$ per cent. from time to time.

Errors are introduced indirectly through the value of $(H\rho)$ assumed for the various lines, and also through the value taken for e/m_0 . With the lines of low energy, these two errors produce effects of the same order, but with very fast rays the former masks the latter.

Summary.—In the foregoing paper, a method of determining the variation of the mass of the electron with its velocity is described. The method consists in the acceleration of the “line” β -rays from RaB and RaC, in a focussing apparatus, and is found to give results of a similar order of accuracy to that obtained by Bucherer in his well-known experiments. The results, using rays of velocity up to 0.8 that of light, agree with the theory of relativity, within the limits of the experimental errors.

In conclusion, I have to acknowledge my indebtedness to a large number of gentlemen for a great deal of help and advice obtained throughout the course of the experiments. My best thanks are due to Prof. Sir Ernest Rutherford, under whose direction the work was performed, and who suggested the experiment, and also to Mr. R. H. Fowler for help with the calculations, and to Dr. Kapitza for much advice. I am greatly obliged to Mr. Crowe for the preparation of the active sources used. Thanks are also due to the Board of Scientific and Industrial Research for a grant.

*The Absorption Coefficient for Slow Electrons in the Vapours of
Mercury, Cadmium and Zinc.*

By R. B. BRODE, Ph.D., Rhodes Scholar, Oriel College, Oxford.

(Communicated by Prof. F. A. Lindemann, F.R.S.—Received July 23, 1925.)

According to the classical dynamics, the molecules in the path of a beam of electrons will, by virtue of their electric fields, deflect the electrons constituting the beam. This deflection, while not perceptible for the electrons which pass at large distances from the molecule, may cause those which approach more closely to disappear from the beam. The effective area, within which an electron will be deflected from the beam, can be calculated from the equation

$$I = I_0 e^{-\alpha x/p},$$

where I_0 is the number of electrons initially present in the beam, I the number remaining at the end of the path x , p the pressure of the gas, and α the absorption coefficient or the effective stopping area of all the molecules in a unit volume of gas at unit pressure. The mean effective area of a single molecule is obtained by dividing α by 3.56×10^{16} , when the units chosen are millimetres of Hg and centimetres. Using this equation, Lenard and others* have determined the absorption coefficients for most of the common gases.

Apparatus.

The apparatus (fig. 1) used in this investigation of α consisted of a filament F, two parallel discs D, 1.2 cm. in radius, and a ring R, 1.3 cm. in radius. The beam of electrons is here replaced by a circular sheet confined between the two parallel discs. The electrons that are deflected in the plane of the discs will reach the ring R, and hence the observed values of α will be smaller than the true value. This decrease, however, is quite small, as the probability of such a deflection is proportional to the solid angle subtended by the opening at the edge of the discs at the point of deflection. This angle is quite small compared to that subtended by the discs.

The bulb in which the apparatus was contained was of pyrex glass. The metal parts of the apparatus were all of nickel except for the tungsten filament and the tungsten seals through the pyrex. It was found necessary to separate

* P. Lenard, 'Ann. der Phys.,' vol. 12, p. 714 (1903); H. F. Mayer, 'Ann. der Phys.,' vol. 64, p. 415 (1921); C. Ramsauer, 'Ann. der Phys.,' vol. 72, p. 345 (1923); R. B. Brode, 'Phys. Rev.,' vol. 25, p. 636 (1925).

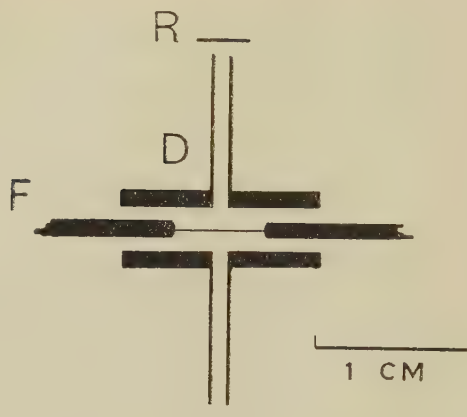


FIG. 1.

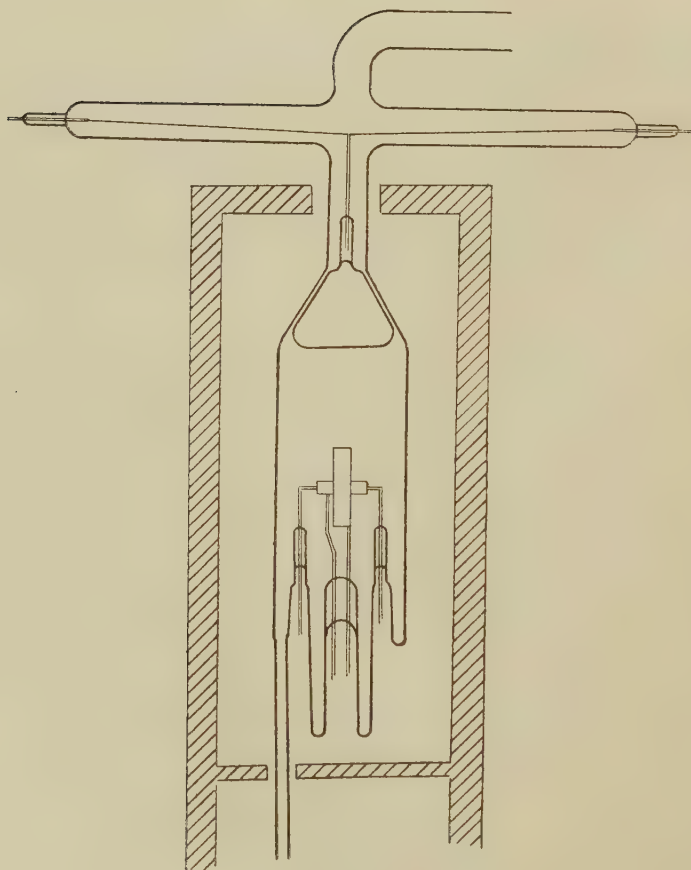


FIG. 2.

the filament seals as widely as possible from the seals for the ring and discs, as at 400° C. there was considerable leakage across and through the glass.

With both cadmium and zinc, in spite of repeated distillation of the metals and the usual baking out of the apparatus and glowing of the nickel parts, gas developed in the bulb after sealing it off. To overcome this difficulty a special valve (fig. 2) was designed to open and close *in vacuo* while in a furnace at 400° to 500° C. The stopper is suspended on a steel wire fastened at the ends to two tungsten seals. When a small current is passed through the wire it sags, because of the heating, and the valve opens. As the pressure used in these experiments was seldom greater than 10^{-2} mm. of Hg, the ground joint alone was found to be quite tight enough when held shut by the spring in the cool-steel wire. With this arrangement the apparatus could be evacuated between successive sets of readings and then sealed off.

Method.

The pyrex glass in which the apparatus was sealed was baked out at 550° C. for four hours, while evacuating continuously. After this the nickel parts were heated to a bright red by bombardment with 1,500-volt electrons from the filament.

The metal used was distilled several times before it was introduced into the bulb. In the case of mercury the apparatus was then sealed off from the vacuum. A small tube, about 15 cm. long, was left on the bulb, and the metal was kept in this. Two air furnaces were used, one for the bulb with the apparatus, and one for the tube containing the metal. The temperature of the furnace containing the apparatus was kept above that of the furnace containing the metal, so that none of the metal would condense in the bulb. Certified mercury thermometers were used to measure the temperature. In order to be sure of good thermal contact between the thermometer and the tube containing the metal they were enclosed together in a small metal container filled with powdered copper.

The filament current was supplied by an accumulator. The voltage drop across the 6-mm. filament when in operation was less than one volt. Consequently, the 1-mm. part of the length supplying the electrons for the ring could be considered as an equipotential source. The midpoint of the filament was maintained at a negative potential with respect to earth. This was done by shunting the filament by a high resistance and fixing the negative wire to a point on the resistance which gave equal electron currents to the ring on reversing the direction of the filament current.

The total emission M of the filament was measured on a micro-ammeter, and was assumed to be proportional to the initial current I . The current I to the ring was measured on a galvanometer. By taking readings at two different pressures the factor of proportionality between M and I was eliminated, and α was computed.

With the temperature of both furnaces constant, the ratio of M_1 to I_1 was observed for velocities of the electrons from 0.4 to 50 volts, 150 in the case of mercury. The temperature of the furnace with the metal was then changed and the value of the ratio M_2 to I_2 again observed. α was then computed from the equation

$$\alpha = \log \frac{M_1}{I_1} \frac{I_2}{M_2} \times \frac{1}{x(p_2 - p_1)}.$$

The pressure p of the vapour in the bulb was obtained from the temperature of the furnace containing the metal by the use of tables of vapour pressure. The data for the vapour pressure of mercury were taken from the values given by Smith and Menzies.* For cadmium and zinc the values given by Egerton† were used. The empirical equations for the vapour pressure as a function of the temperature are :—

$$\text{Zinc} \quad \dots \quad \text{Log } p = 9.284 - 6997.7/T.$$

$$\text{Cadmium} \quad \dots \quad \text{Log } p = 8.934 - 5891/T.$$

$$\text{Mercury} \quad \dots \quad \text{Log } p = 9.907 - 3276.6/T - 0.652 \log T.$$

Results.

The values of the absorption coefficients for mercury, cadmium and zinc are shown in figs. 3, 4 and 5. The value of the absorption coefficient in square centimetres has been plotted against the square root of the voltage. The observations in mercury were carried to 150 volts, and the value of α was found to decrease uniformly from 22.5 at 50 and 11.5 at 100 to 4.5 at 150 volts.

In the observations on mercury, a large number of readings were taken at 19.0° C. ($p = 0.0012$ mm. of Hg), and the mean of these was taken for the ratio I/M . Readings were then taken at temperatures where p_2 was 0.0030, 0.0106, 0.0195, and 0.0312 mm. of Hg. The values plotted have been corrected for the temperature of the furnace containing the apparatus. The values of α are for 1 mm. of Hg pressure at 0° C.

There appeared to be no other gases or vapours in the tubes, since their appear-

* A. Smith and A. W. C. Menzies, 'Ann. der Phys.,' vol. 33, p. 979 (1910).

† A. C. Egerton and F. V. Rayleigh, 'Trans. Chem. Soc.,' vol. 123, p. 3024 (1923).

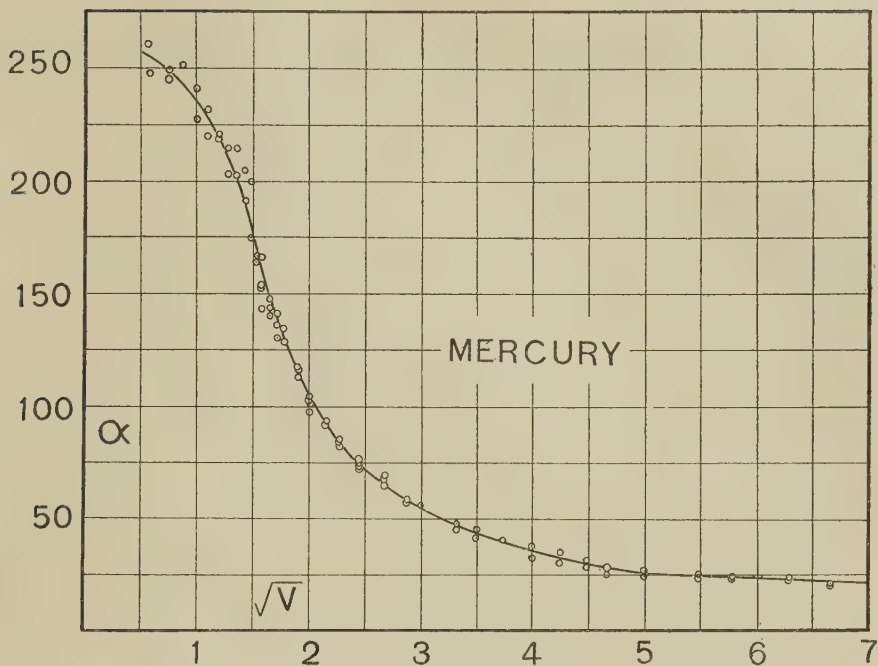


FIG. 3.

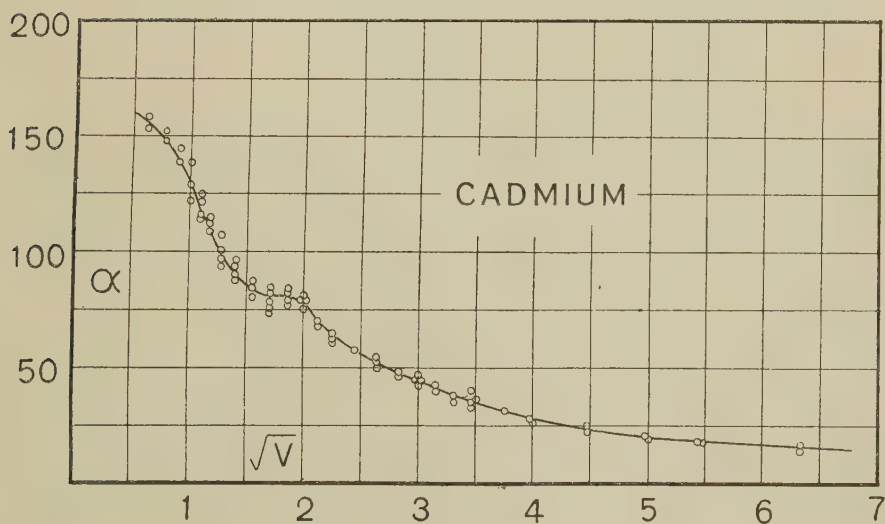


FIG. 4.

ance would have given inconsistent values for the α 's determined at different temperatures, unless the vapour pressure constants of the impurities were the same as those of the metal. No gases were given out by the walls and

metal parts, as readings taken three months apart with the sealed-off mercury tube gave the same values of α , and readings taken two hours after closing the valve with cadmium and zinc gave unchanged values of α .

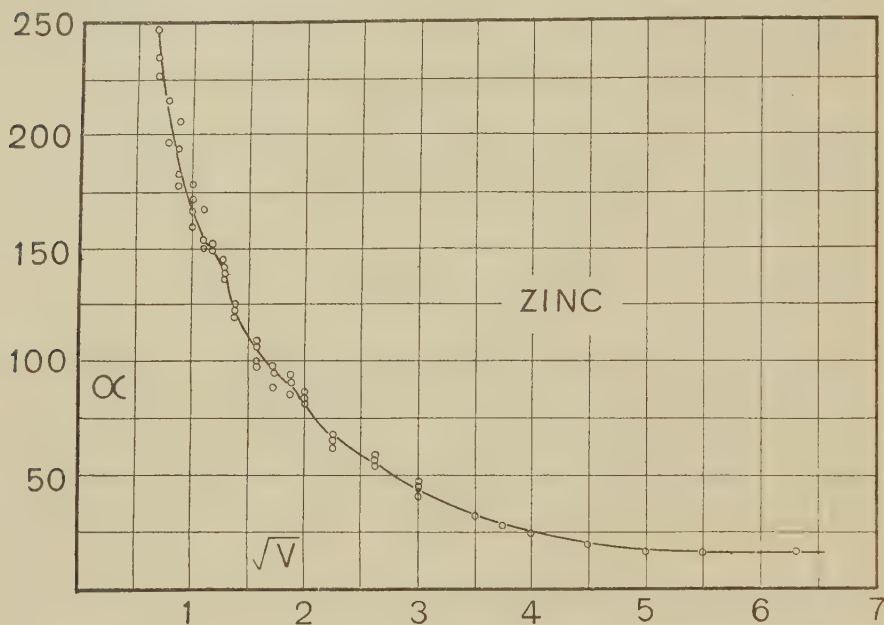


FIG. 5.

When the voltage was increased beyond the ionisation potential, the value of α suddenly decreased. If p_1 was zero and p_2 small, the value of α was often negative. This indicated that with the same total emission from the filament, more electrons were reaching the ring when the space was filled with gas molecules than when it was empty. As the pressures p_1 and p_2 were increased, the value of α became positive, and above 0.03 mm. of Hg pressure the value of α was nearly independent of the pressure.

This phenomenon seems to be due to the effect of the positive ions on the emission of the filament. In the field-free space between the discs positive ions are formed, and some of them drift towards the centre of the discs where they are then drawn towards the filament. These positive ions about the central part of the filament reduce the space charge there and increase considerably the emission of that part which furnishes the current to the ring. Most of the electrons from the filament to the discs pass directly to the guard cylinders on the discs. These electrons will only have acquired sufficient energy to produce ions at the very end of their path. The number of positive

ions produced along the rest of the filament will therefore be very small, and the current to the discs M will not increase as rapidly as I, thus causing negative values of α .

The thickness of the layer, within which ionisation may take place, increases with the velocity of the electron. The increasing number of positive ions tends to equalise the emission along the filament. For this reason the variation in the values of α should disappear at high velocities. The observations on mercury showed a maximum discrepancy in the readings at 20 volts, while at 50 volts the effect had entirely disappeared.

If the value of α is determined with two relatively high pressures, the disturbances due to ionisation will be nearly the same in both cases, and the change in the current to the ring can be attributed to the effective stopping area of the additional molecules. The values of α plotted for voltages above the ionisation potential were observed with pressures of the metal vapour above 0.02 mm. of Hg pressure.

If the filament is made quite short, so that most of the current to the discs comes from the same part of the filament as that supplying the ring, the effect of passing the ionisation potential will be less marked. This was tried in the apparatus with cadmium, and very little effect was observed when the ionisation potential was passed.

Discussion.

Considerable variation in the values of α at any one voltage might have been expected, as the pressure was determined from the temperature and the vapour pressure curve. An error of a few degrees between the actual temperature of the bulb containing the metal and the temperature observed would have produced a large error in the pressure and consequently in the value of α . The good agreement of the observations at different temperatures indicated that the thermometer was reading correctly the temperature of the metal.

Because of the phenomena of secondary emission and reflection from bombarded metal surfaces, one cannot be certain that all of the electrons arriving on the ring have come in a straight path from the filament. Errors from this source were eliminated as far as possible by keeping the electron current constant for each set of readings, the density of the vapour alone being varied.

In a paper on the free path of electrons in mercury and cadmium, R. Minkowski* concludes from the effect of space charge on the emission curve of a

* R. Minkowski, 'Zeit. f. Phys.,' vol. 18, p. 258 (1923).

filament, that there is a small increase in the free path for velocities less than one volt. The method used by Minkowski was not capable of giving numerical values for the free path.

The reciprocal of the absorption coefficient, α , is the free path at a pressure of 1 mm. of Hg. The actual observations do not indicate any long free paths, but on the contrary give very small free paths for values of the velocity as low as 0.4 volts. The rate of decrease of the free path in mercury and cadmium became less below one volt, but no minimum was observed. It appears that the small effect observed by Minkowski must be due to some other cause. From a recent theoretical paper by Hertz* it appears that in dealing with problems of diffusion of electrons in gases, the shape of the apparatus plays a very much larger part than was previously assumed. It is therefore possible that the small variation in the diffusion in Minkowski's apparatus should not be assigned to a variation in the free path, but to an effect of the geometry of the apparatus.

With the exception of the drop in the curve for cadmium below 4 volts, the curves for the three metals are of the same magnitude and shape. They approximate closely to a hyperbolic curve as given by the theory of Zwicky,† for the deflection of an electron in the field of a molecule due simply to the polarisation by the field of the electron.

From the effective quantum numbers for the outer electrons the size of their orbits can be estimated, and this gives values of α of about 20 for these metals. Nettleton‡ has measured the effective area for ionisation of the mercury molecule at 100 volts. The α (ionisation) is 12.0 at 100 volts, while in this investigation the α (deflection) is 11.0. These data indicate that for high velocities the electrons can come closer to the body of the atom than the normal orbit of the outer electrons and still not suffer a deflection. When they do suffer a deflection they also ionise the molecule.

The kinetic theory value of the effective area of mercury molecules is given by* Koch§ as $\alpha = 88$ for molecules moving with the mean velocity at 0° C. At 300° C. the value of α is 18.

Summary.

The absorption coefficient, or the effective area of a molecule within which an electron is deflected, was measured for electrons from 0.4 to 50 volts velocity in the vapours of mercury, cadmium and zinc. Except for the change below

* G. Hertz, 'Zeit. f. Phys.,' vol. 32, p. 298 (1925).

† F. Zwicky, 'Phys. Zeit.,' vol. 24, p. 171 (1923).

‡ L. L. Nettleton, 'Proc. Nat. Acad. Sci.,' vol. 10, p. 140 (1924).

§ Koch, 'Wied. Ann.,' vol. 19, p. 857 (1883).

4 volts in cadmium, and the small drop in mercury below 3 volts, the curves are approximately hyperbolas of the same size. No indications of long free paths at low velocities were found.

The sudden decrease in the absorption coefficient above the ionisation potential, when measured at low pressures, is shown to be due to the effect of the ions on the emission of the filament and not to a true change in the absorption coefficient.

A type of valve is described for closing off the apparatus *in vacuo* at high temperatures.

It is with pleasure that I thank Prof. Lindemann for extending to me the facilities of his laboratory and for his interest in the problem. I am also indebted to Mr. Egerton for furnishing me with samples of pure zinc and cadmium, as used by him in the determination of vapour pressures.

The Structure of α and β Quartz.

By SIR WILLIAM BRAGG, F.R.S., and R. E. GIBBS.

(Received July 29, 1925.)

The quartz crystal has a trigonal axis and three digonal axes, which are at right angles to the trigonal axis. It has no other element of symmetry. It belongs to Class 18 of the 32 classes into which crystals may be divided by their outside appearance. It was shown in 1913,* by the methods of X-ray analysis, which were then new, that the unit cell contains three molecules of SiO_2 , which are so arranged that a revolution of 120° round the principal axis, coupled with a translation $c/3$ along it, brings each molecule into the exact position previously occupied by one of its companions. The trigonal axis is in fact a screw axis. The value of c is 5.375 A.U. The distance between an axis and each of its six equidistant neighbours is 4.89 A.U. Each silicon molecule possesses a digonal axis. This particular arrangement of molecules is known in mathematical crystallography as that of the space-group D_3^4 or D_3^6 , according to the rotatory sense of the lattice.

At this stage of the work four parameters still remained to be determined

* 'Roy. Soc. Proc.,' A, vol. 89, p. 575.

before the positions of the atoms in the crystal structure could be defined. The position will be clear from a consideration of fig. 1, which is reproduced from

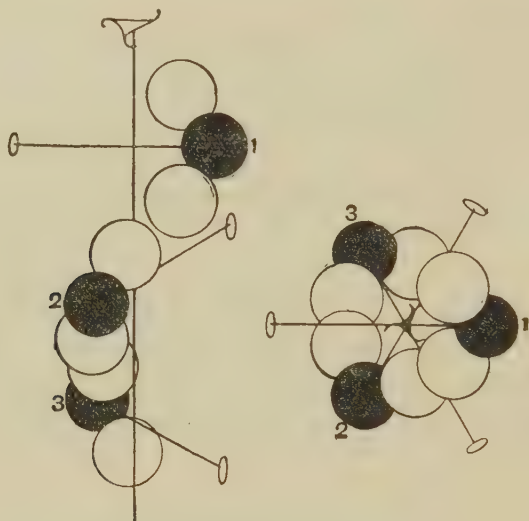


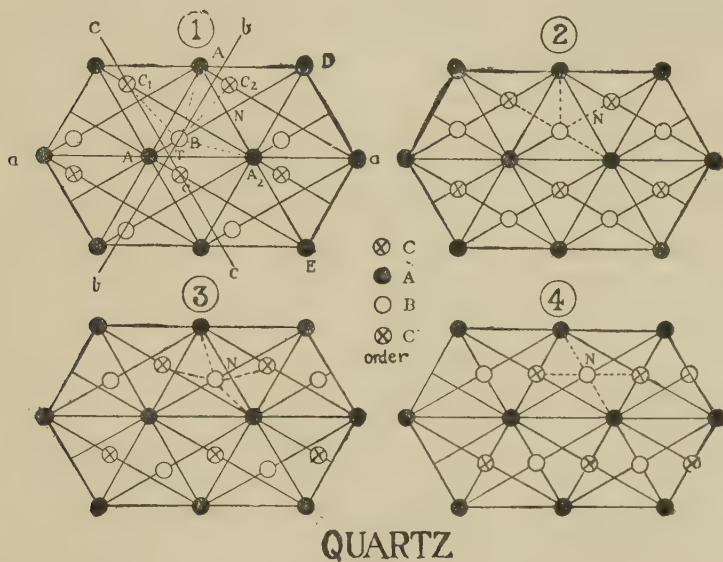
FIG. 1.

'X-rays and Crystal Structure,' p. 261. Each of the two diagrams in the figure shows the relation between three molecules, forming the content of the unit cell, and derivable from each other in the manner described. In one, the screw axis is in the plane of the paper, in the other at right angles to it. The diagonal axes are also shown. The distance of the silicon (black disc) from the axis is one of the unknowns: the spatial relations of the oxygens to the silicons require for their definition three more. The diagram of fig. 2 shows various possible positions of the silicon atoms when projected upon the basal plane. They must lie on certain lines, as shown, in order to satisfy the symmetry conditions.

If the principles governing the intensities of reflection of X-rays by the crystal planes were sufficiently understood it would be possible to determine the four unknowns by intensity considerations alone. But this is not yet the case, and some new principle must be called in to direct the attempt at finding a solution. The intensities can be used later on as a test of the result.

There is just one case in which the intensity measurements give a clear indication. The relative spacings of the atom-bearing planes which can be drawn perpendicular to the principal axis can be understood from fig. 1. Each silicon plane has two oxygen planes at equal distances on either side of it. The distance between two consecutive silicon planes is known; it is 1.79 A.U. But the distance between a silicon plane and either of the neighbouring oxygen

planes is not known ; let it be denoted by d . Now the intensity measurements show that d must be a considerable fraction of the distance between the two



QUARTZ

FIG. 2.

silicon planes. The first, second and third orders of the reflections from the basal plane are all weak. If d were zero, the first order would be exceedingly strong compared to the others ; if it were half the distance between two silicon planes all the odd orders would be very small ; if it were one-third of the distance the first and second orders would be very small compared to the third. It is probable that d is somewhere between a third and a half of the silicon spacing. It is almost impossible to find an exact value because the silicons and oxygens scatter differently at different inclinations to the primary beam according to rules imperfectly known. If the scattering powers of silicon and oxygen had to be assumed to be proportional to their atomic weights for all angles of scattering, no value of d would explain the observed ratios of the first, second and third orders very closely. It is necessary therefore to be content with the approximation suggested, which is, nevertheless, a very useful one.

Various principles have been suggested at different times in order to remedy the defect of the intensity measurements. Huggins and McKeehan have suggested structures which satisfy certain plausible chemical considerations. But these workers both place the oxygens in the same planes, normal to the principal axis, as the silicons ; and, as we have seen, there is the strongest evidence that

this is not the case. Sosman has developed a proposal by Beekenkamp, in which the silicons are placed as in the second variation of fig. 2, but it is difficult to reconcile this particular hypothesis with the symmetry requirements of β - or high temperature quartz. In 'X-rays and Crystal Structure' it is suggested that each silicon atom is in contact with two neighbouring silicon atoms of the same spiral, and that the lines joining its centre to those of its two neighbours make with each other the tetrahedral angle of $109^{\circ} 28'$; but this hypothesis is not adopted in what now follows.

There is no great certainty in the action of any of these principles, nor any great measure of satisfaction in the results. The object of this paper is the description of a new method* of arriving at a solution, which seems much nearer the truth, since, in the first place, it gives a satisfactory account of the intensity measurements and in the second it explains many of the physical properties of quartz, such as its varied twinnings. It is based on the fact that at 575°C . ordinary quartz (α quartz or "low" quartz) passes from the trigonal to the hexagonal form. Good reason may be given for supposing that the positions of the atoms are very slightly altered in the transformation. Now the hexagonal quartz (β quartz or "high" quartz) is simpler than α quartz, and the four unknowns reduce to one. The intensity measurements can be satisfactorily employed in the determination of the last unknown. When the structure of β quartz has been found, then, because the difference between α quartz and β quartz is small, the determination of the actual structure of the former becomes much simpler than before. Let us take these points in order, and in the first place let us consider the phenomena attending the transformation from α to β quartz.

In 1889, Le Châtelier (*C.R.*, vol. 108, p. 1046) showed that the coefficient of expansion of quartz, both along and across the axis, underwent a sharp change at about 570°C . His figures are given in the following table. The quantities set down are the actual increases in mm. of the length of a specimen, which had an initial length of 100 mm. at 15°C .

It is to be observed that below 570° the quartz expands more rapidly across the axis than along it, and that above 570° there is very little change in length in either direction for a great increase in temperature. The actual change is rather a contraction than an expansion, is very small, and is much the same for both. There are no considerable changes in dimensions near the critical point; which fact suggests that there is no radical alteration of structure. So

* A preliminary account of this method was given in the course of a series of lectures delivered at the Royal Institution, February, 1925.

	Parallel to axis.		Perpendicular to axis.	
	1st Experiment.	2nd Experiment.	1st Experiment.	2nd Experiment.
°				
15	0	0	0	0
270	0.20	0.33	0.43	—
480	0.53	0.55	0.82	0.86
570	0.93	0.93	1.30	1.45
660	0.95	0.99	—	1.59
750	—	0.95	—	1.59
910	0.90	0.87	—	1.57
990	—	0.86	—	1.57
1060	—	0.89	—	1.55

also the measurements of the specific heat of quartz made by Perrier and Wolfers ('Arch. des Sci.,' 1920, p. 372) show that there is a sharp change at the critical point in the relation between specific heat and temperature, and further that there is a definite absorption of heat amounting to four gramme calories during the passage over a narrow range which includes the critical point. The smallness of the latent heat is a further indication of the slight character of the structural change.

The rotatory power behaves in the same way. The rate of variation with temperature undergoes a sudden change in passing through the critical point, and at the same time there is, according to Le Châtelier, a sharp though small alteration in the quantity itself.

The exact measurements which can be made with the goniometer show the same effect in yet another way. F. E. Wright and F. Rinne have made independent measurements of the temperature variation of the angle between two adjacent pyramid faces on the quartz crystal. Rinne's curve* is here reproduced (fig. 3). The alteration in angle is a consequence of those changes in linear dimensions which Le Châtelier measured directly, as explained already.

Rinne also gives (*loc. cit.*, p. 166) a curve, reproduced in fig. 4, which shows the changes in refractive index of the ordinary and extraordinary rays.

There is a temporary double refraction as quartz passes from one phase to the other: this is probably due to strain resulting from unequal expansions.

The value of Young's modulus at various temperatures has been carefully determined by Mandrot ('Elasticité et Symétrie du Quartz aux Températures élevées,' Lausanne, Imprimeries réunies, 1924). The results are very definite,

* Rinne, 'Crystals and the Fine Structure of Matter,' p. 167.

and form one of the most satisfactory means of watching the effects under consideration. His curves, here reproduced in fig. 5, show the changes in

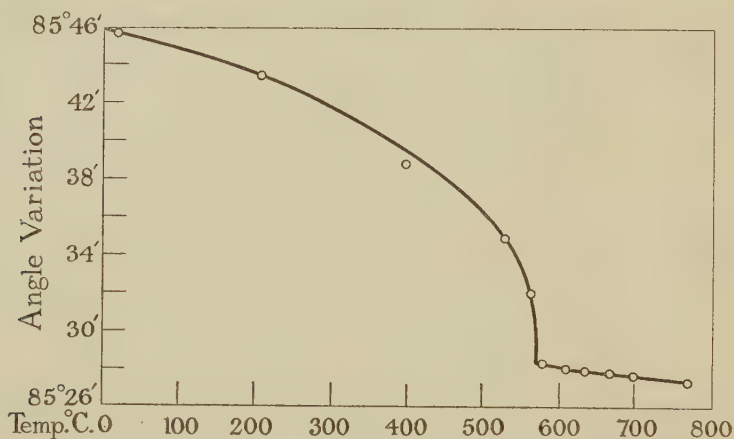


FIG. 3.

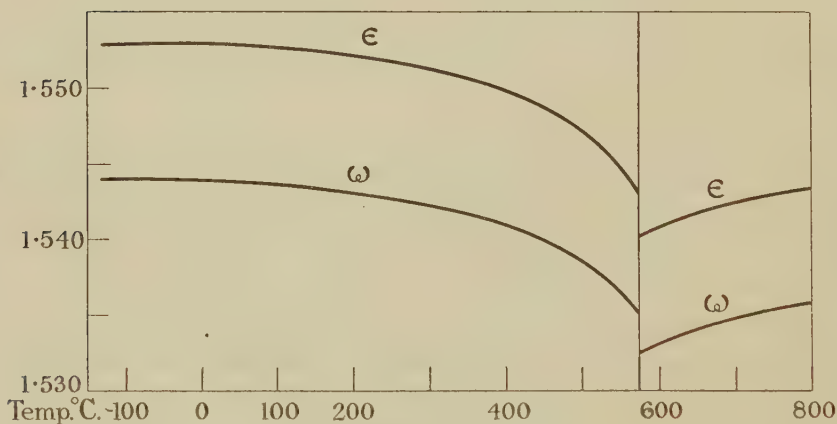


FIG. 4.

Young's modulus over a wide range of temperature; the critical point is exceedingly well marked, and, as Mandrot says, the sudden drop in the modulus at 575° may well be more marked even than is shown by the curves.

R. E. Gibbs ('Proc. Roy. Soc.,' A, vol. 107, p. 561) has measured the intensity of reflection of X-rays by various planes in the crystal. The experiments were undertaken in the hope of showing some effects of the movements of the atoms, of which the reflections are an extremely sensitive indicator. Some planes and some orders were found to give sharp and sometimes considerable changes in intensity at the critical temperature; others gave very little. Naturally, the

differences would be due to the greater movements of the atoms across the former planes than across the latter. In particular, the second-order reflections

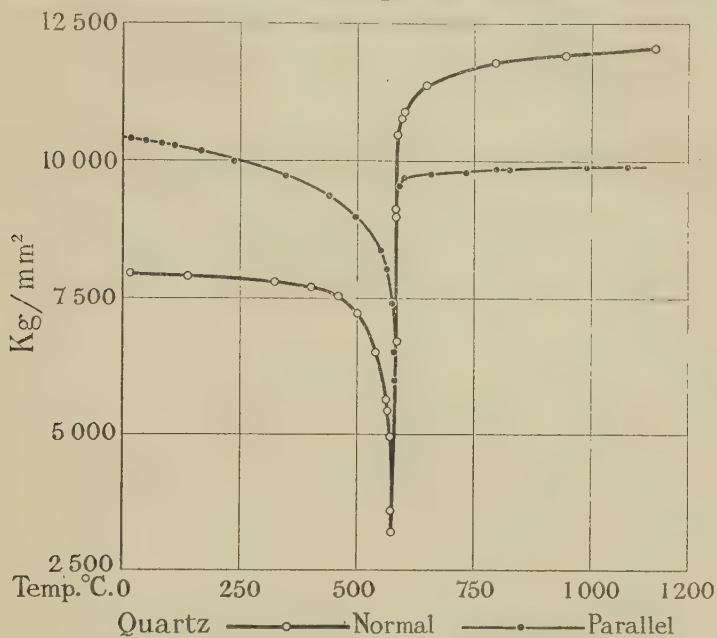


FIG. 5.

from the basal (111) plane and the $1\bar{1}0$ plane were much affected. The former effect is illustrated in fig. 6 ('Proc. Roy. Soc.,' A, vol. 107, p. 565, graph 4), which

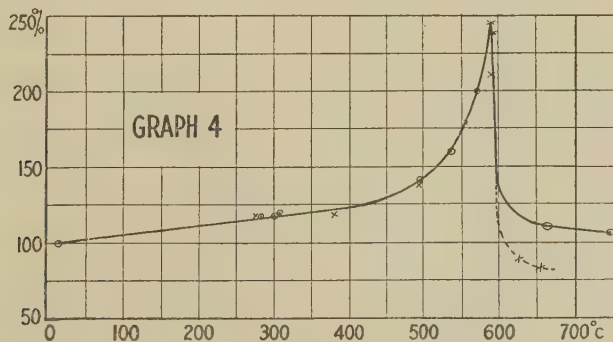


FIG. 6.

is repeated from the paper quoted. These measurements also showed clearly the more general point that there is no great change of structure in the α , β transformation; the chief reflecting planes in the one case were found in the other with very little difference in their spacings. Even the considerable alterations in intensity could be explained by quite small atomic movements.

The general conclusion to be drawn from the preceding summary is that there is a well-defined critical temperature, at which the atoms take up a new arrangement, almost as suddenly, it may be, as a lock turns over at the last. But the atomic movements are not large; certainly not large enough to cause a marked change in the structure of the crystal.

The next point to be considered is the symmetry of β quartz. It differs from α quartz in that it possesses six digonal axes instead of three, all perpendicular to the principal axis. It is a hexagonal crystal, whereas α quartz is only trigonal. The three digonal axes of α quartz pass through the edges of the quartz prism: the three new axes are perpendicular to the faces. Let us examine the evidence for this statement.

In the first place, the Laue photographs show clearly the increase of symmetry from the trigonal to the hexagonal. Those given by Rinne (*loc. cit.*, p. 71) for a plate cut perpendicular to the principal axis show six intersecting lines of symmetry above 575° C. and only three below. His figures are here reproduced (fig. 7). It may be helpful to point out that, though there

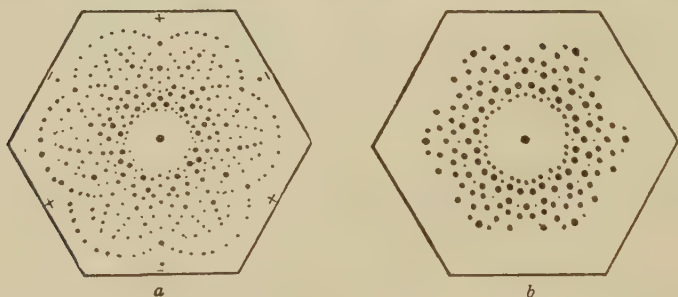


FIG. 7.—*a* and *b*. Laue diagrams of α quartz and β quartz. After F. Rinne.

are no planes of symmetry in the quartz crystal, symmetry naturally appears in the Laue photograph. If the hexagon in the figure (fig. 8) represents a section of the quartz prism perpendicular to the axis, planes through AB, CD, EF and intersecting on the axis, above the plane of the paper, are exactly like one another, both in spacing and in the distribution of the atoms with respect to them. If the incident X-rays are directed along the axis, the rays reflected by the different series of planes form similar series of spots along OP, OR and OT, respectively, and those along OP and OR, for example, are mirror images of each other across QT. But the reflections of the corresponding planes through BC, DE and FA, though similar in position to the reflections from those through AB, CD and EF, since the spacings are the same, differ in respect to their intensities. In β quartz the six series of spots are

all alike ; and the photograph shows a hexagonal instead of a trigonal arrangement.

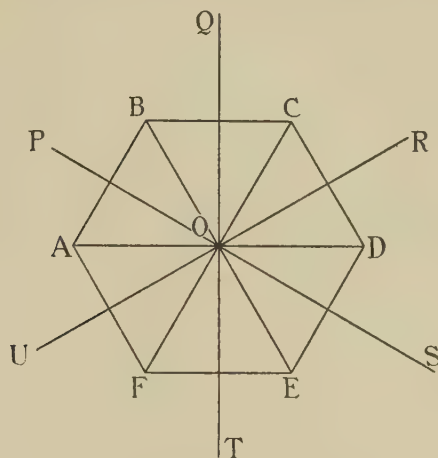


FIG. 8.

A very sensitive test of the same point is furnished by the elasticity experiments of Mandrot (*loc. cit.*). Two plates of quartz were cut, making equal angles (50° in this case) with the axis, on opposite sides of it ; the intersection of the plates was normal to the axis. A value of Young's modulus was found for each plate by the bending method. In the case of α quartz the values for the two sections were quite different ; above the transition point they became identical. The changes are clearly shown in Mandrot's curves, reproduced in fig. 9. We may here remark again how low the elastic constant becomes at the critical point, and how very suddenly it recovers.

As a third demonstration of the change, we may take the disappearance of the piezo-electric effect above the critical temperature (Perrier, 'Arch. Sci. Phys. et Nat.,' vol. 41, p. 493). Its existence cannot accompany the increase of symmetry.

Again, we have made single-crystal rotation X-ray photographs of quartz, first at ordinary temperature and then well above the transition point at about 700°C . The photographs, which record practically all the reflections that are geometrically possible, are surprisingly similar ; only small changes having occurred in the intensities, and no more than the usual expansion changes in the spacings.

It is to be observed that while the β rotation photographs permit of direct interpretation those for the α state are composite pictures, in which the reflections include two types of faces which have the same spacings. For example

the reflections from both types of pyramid face are superimposed, and only an average result is shown. This partially explains the similarity which we

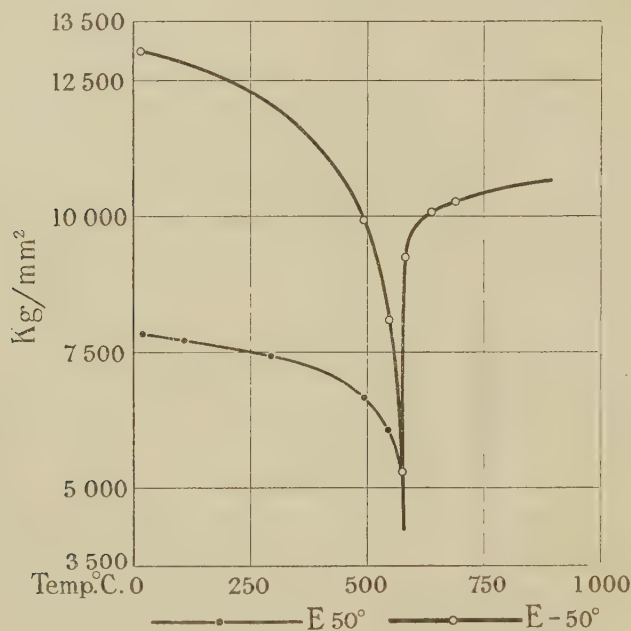


FIG. 9.

have found, but, even so, it is at once clear that the two structures must be closely allied. The spacing of the 0001 plane is still divided into three, as in α quartz.

There is therefore ample evidence that β quartz is hexagonal. Optical activity persists, but piezo-electricity disappears. The symmetry is that of Class 24; the "space group" of mathematical crystallography is D_6^4 , or D_6^5 , according to the rotatory sense of the lattice.

The X-rays show that the changes in the dimensions of the unit cell are only such as are due to the slight expansion; there are still three molecules in the cell, arranged in the same screw fashion. But the increased symmetry reduces in a drastic way the permissible variations in atomic position. To begin with, of all the variations of which examples are given in fig. 2, the fourth diagram shows the only possible positions of the projections of the silicon atoms on the plane normal to the axis. For it is now necessary that the figure should show symmetry, not only across the horizontal line in the plane of the paper, but also across the vertical line in the same plane.

There is, indeed, one other arrangement which would satisfy the symmetry

considerations. It is an extreme case of the variations of fig. 2, and is not shown as one of the four examples. In this, silicons are in rows parallel to the principal axis; the three projections A, B, C of fig. 2 coincide. But this seems an impossibility for structural reasons, since the distance between the centres of two neighbouring silicon atoms in the same vertical row would be 1.80 A.U. only; whereas in the silicon crystal, which is a tightly-bound construction, the distance is 2.35 A.U. At the same time, the shortest distance between the axes of two neighbouring silicon rows, being 4.89 A.U., would be much too large to be bridged, even with the help of the oxygen atoms. Rejecting the latter alternative, therefore, we adopt the former as the only possible solution. The positions of the silicon atoms in β quartz are determined, and it remains only to place the atoms of oxygen.

Now the symmetry conditions are so strict as to leave even these very little freedom. For consider the projection of the silicon atoms at which we have now arrived; let it be divided up into hexagons as in the figure (fig. 10). Three silicon atoms belong to each hexagon, since each atom belongs to two neighbouring hexagons, and there are six atoms to the six sides. There are twice as many oxygen as silicon atoms in the crystal, so that there are six oxygens to each hexagon. Their projection on the plane of the diagram must also lie at the corners of a hexagon as shown by the small circles, since the symmetry is hexagonal. The hexagon might lie, so far as symmetry compels, in either of two ways, fig. 10 (a) or 10 (b), since in both cases the oxygen hexagon is symmetrical about each of the six projections of the diagonal axes.

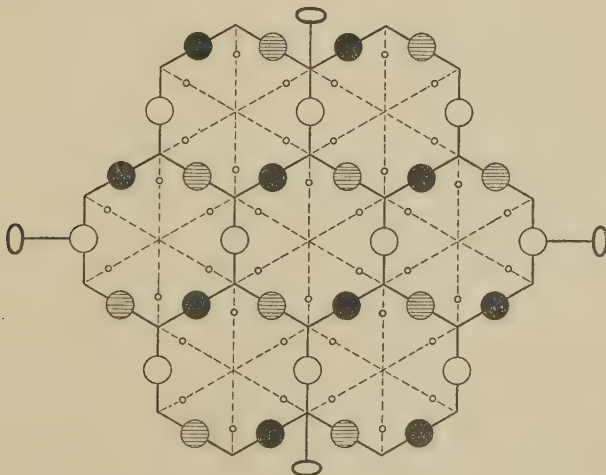


FIG. 10a.

There are, however, serious objections against the second arrangement. As already mentioned the large black spots represent silicon atoms in the plane of the paper, the empty circles are the projections of silicon atoms lying in a plane which is at a height above the paper equal to $c/3$; the shaded circles represent, correspondingly, silicon atoms in a plane $c/3$ lower than the paper. Consider the digonal axis. The oxygen atoms p and p' must lie either (a) on the axis in the plane of the diagram, or (b) half-way between successive digonal axes, at a distance $c/2$ above and below the plane. In the exceptional case when p and p' coincide with P in the diagram, symmetry conditions are satisfied if p and p' are at any equal distances above and below P. But the lines ...O.Si.O.O.Si.O...which are thus formed parallel to the axis are quite out of reach of each other, so that this construction is impossible. In case (a) the oxygens all lie in silicon planes, and, as we have seen, this is impossible in view of the intensities of the basal plane reflections. In case (b) the distances between silicon and oxygen are much greater than we are led to believe from all the evidence that we have. The oxygen marked p cannot be nearer to the silicon P than by the distance $c/2$ or 2.7, nor can it be nearer to Q than $\sqrt{(2.1^2 + 0.9^2)} = 2.3$. For the shortest distance between the axis and Q in the plane of the paper is 2.1, and the difference in level is 0.9. We suppose the oxygen and silicon atoms to be bound together tightly in such a crystal as quartz, and expect the distance between them to be much less than 2.3. This is the distance between the atoms in silicon itself. In calcium carbonate the distance between carbon and oxygen is 1.25 A.U. ; it is not to be expected

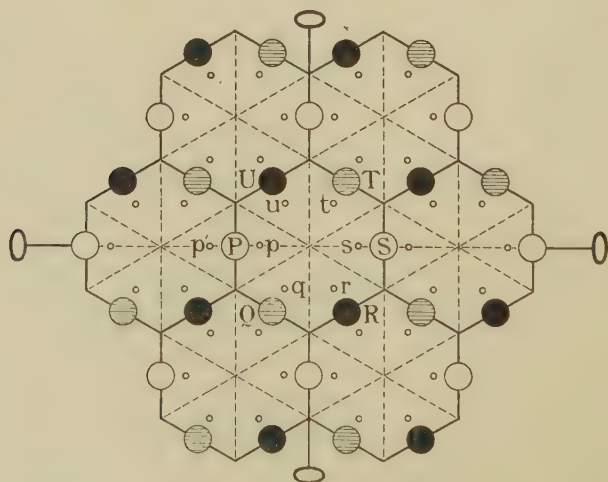


FIG. 10b.

that the substitution of the silicon for the carbon radius should add a whole Ångström Unit to the distance between the neighbours.

These objections seem to rule out fig. 10 (b), but they do not hold against fig. 10 (a).

We now consider the relative vertical positions of the oxygens. In fig. 11 the silicons of a single hexagon are denoted by large circles, in which are placed figures 0, 1 or -1 . Those marked 0 lie in the plane of the paper; those marked $(+1)$ in the plane $c/3$ above it; those marked (-1) in the plane $c/3$ below. If the height of one of the oxygens above the plane of the paper is

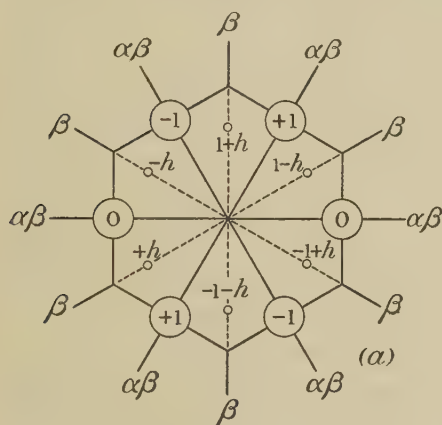


FIG. 11a.

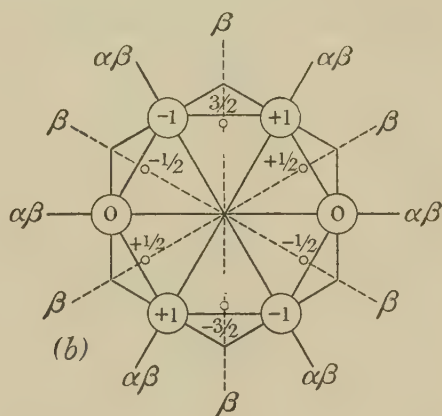


FIG. 11b.

denoted by h as in the figure, the heights of the other five in the hexagon can be written down at once in accordance with the conditions of digonal symmetry about the axis which is the horizontal line in the figure, and about the other two axes like it; these three are digonal axes of both α and β quartz. In addition the vertical line in the figure must also be a digonal axis; the two axes which project in the figure into two lines making 60° with the vertical line are the other two digonal axes which β quartz possesses (but not α quartz). In order to satisfy this condition h must be equal to $1/2$. In the right-hand hexagon of the figure this substitution is actually made.

There is now only one undetermined parameter, which may be stated as the distance of each oxygen, in the plane of fig. 11 (b) from the nearest side of the inner hexagon which joins together the projections of the silicon atoms. If this distance vanishes, each oxygen lies in a straight line between two silicons. In order to determine the value of this quantity which we may term x , recourse may be had to the intensity measurements, and this we have done. Calculation

is still a little lengthy, but with only one parameter it is effective ; when there were four parameters, and there was no assistance from other considerations, it was practically impossible.

After some experimental difficulties had been overcome an apparatus was set up to maintain the crystal at a temperature of about 700°C . over a period of several hours and photographs were taken of the β quartz. The intensities of the reflected spots were estimated, and after allowances, necessarily very approximate, had been made for the number of planes effective during a rotation, for the variation of intensity with glancing angle, and for the sensitivity of the photographic plate, the amplitudes appeared as proportional to the following values for a plane h, k, l, m :—

m	$22\bar{4}m$	$11\bar{2}m$	$12\bar{3}m$	$3\bar{3}0m$	$2\bar{2}0m$	$1\bar{1}0m$
3	0	0	12	0	45	3
2	5	41	21	16	9	7
1	0	0	20	16	13	37
0	5	14	0	4	16	11

The values are not in any sense to be considered as really accurate, but are given as indicating only the order of intensity of the reflections.

It was of some assistance that in each set of planes of the series $n\bar{n}00$, $nn\bar{2}n0$, $n2n\bar{3}n0$, the alternate planes are twice as rich in silicon atoms as the rest of the set. The relative intensities of the different orders of reflection should therefore be the same for each set so far as the influence of the silicons is concerned, and the positions of the oxygens can alone cause any differences between the different sets. It is not necessary to enter into the full calculation here, but merely to give the results obtained.

The $1\bar{1}01$ and the $2\bar{2}01$ were good planes to study as, in the former case particularly, the intensity ratios were very sensitive to a change in the value of the parameter x . It was first shown that no satisfactory solution could be obtained unless the oxygens lay within the inner hexagon of fig. 11 (*b*). Next, an upper limit for x equal to one-eighth of the distance between opposite sides of the hexagon could be set with certainty. By consideration of the $1\bar{1}00$ for which reflection diminishes fairly rapidly with increase of x , and at the same time of the $1\bar{1}03$ for which intensity increases with x at about the same rate, x could be shown to be between one-sixteenth and one-eighth of the distance mentioned ; the value about one-twelfth gives a general agreement with the observed intensities for all these planes. The planes $12\bar{3}n$ agree reasonably well, and it is only in the $mm\bar{2}mn$ series that for one plane 2242 the agreement is

not good. Thus we may say that as far as intensity results are able to help, the value of x is near one-twelfth of the distance between the opposite sides of the hexagon, its actual value in A.U. being therefore $4.23/12 = 0.35$ A.U.

Before proceeding further it is advisable to repeat that the problem of estimating and accounting for intensities is beset with so many uncertainties that only approximate results can be expected. In the above calculations the reflecting powers of the oxygen and silicon atoms are taken as proportional to their atomic weights. The error introduced in doing this will affect, more particularly, the intensities of the planes of smaller spacing in which it has been shown theoretically by Hartree* that the oxygen atoms are relatively less effective as the angle of scattering increases, and can finally be almost neglected in comparison with the silicons. It is desirable therefore to seek any additional evidence in favour of the special structure so obtained. Now it is surely significant that the value which we have found for x , viz., 0.35 A.U., is very nearly equal to a particular value 0.33 A.U., which places the oxygens almost exactly in a tetrahedral arrangement around the silicons. This is a very striking result. It is in agreement with the fact that silicon, being a tetravalent atom, is probably striving for such an arrangement.

The spirals parallel to the principal axis are formed by alternate atoms of silicon and oxygen. A little consideration of atomic diameters shows that here, again, the structure is in general agreement with previous results. The distance from an oxygen to any of its six oxygen neighbours is 2.55 A.U., which compares with 2.75 A.U. in the case of water, where the force drawing the oxygens together is due to a singly charged hydrogen; here it is due to a quadruply charged silicon. The distance from silicon to oxygen is 1.55 A.U., which compares with 1.25 A.U. for the distance of carbon from oxygen in calcite, leaving a difference of 0.3 A.U. to be accounted for by the change of atomic radius from carbon to silicon. Lastly, the distance from one silicon to the next is 3.034 A.U.

In this structure each silicon is surrounded by four oxygens and each oxygen touches two silicons, and it is of interest to note that the two oxygen bonds are not collinear but staggered at an angle of about 155° .

Suppose a cube to be drawn round each silicon so that the four oxygens surrounding the silicon lie at four corners of the cube. The projection of this structure upon a plane normal to the axis gives the diagram of fig. 12, in which each corner of a square corresponds to the projection of an oxygen atom. The three different types of shading denote the progressive stages of the cubes along

* 'Phil. Mag.,' vol. 50, p. 289 (1925).

the axis. There is a spiral of large diameter round the empty hexagon, another of small diameter round the empty triangle. If the side of a square is denoted

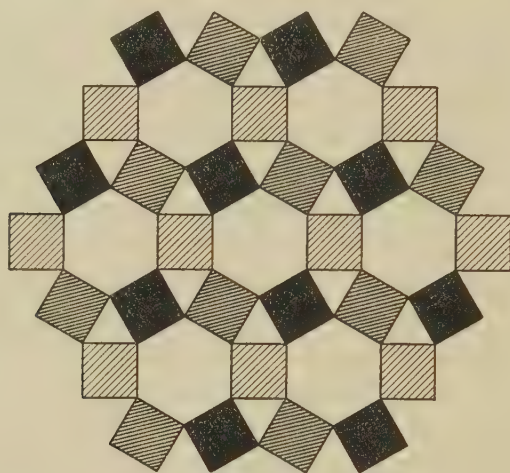


FIG. 12.

by s , then the crystallographic " a " being the least distance between the centres of two like squares in the diagram is $s + s\sqrt{3}$, and the crystallographic c is the height of three cubes, *i.e.*, $3s$. Hence the ratio $c/a = 3/(1 + \sqrt{3}) = 1.098$. This figure relates to β quartz; if a slightly uncertain allowance is made for the greater contraction across than along the axis during cooling this ratio must be increased somewhat to give the value of c/a for α quartz. Using Le Châtelier's figures, the ratio becomes about 1.1025. Tutton gives 1.1000 as the result of very careful goniometric measurements. The agreement between these figures is close, but perhaps not quite so close as it ought to be. The point may be put in another way. If $c/a = 1.098$, the rhombohedral angle should be $85^\circ 41'$. According to fig. 5 it is $85^\circ 29'$, and the difference is rather large to be ascribed to experimental error.

We have now reached, assuming the correctness of our arguments, a complete determination of the structure of β quartz. As has been stated above, the structure of α quartz must resemble closely that of β quartz, the difference involving only small movements of the atoms. It is important to observe that these movements, since they imply a loss of symmetry, may take place in either of two opposite ways as the crystal in cooling passes through the critical temperature. The arrangement of the silicons in plan, as shown in fig. 10 (*a*), may be modified into either the form shown in fig. 13, or the same form turned round 180° in its own plane. The horizontal direction in the paper and two lines

inclined to it at 60° are the directions of the digonal axes, which are also the electric axes. If the crystal is compressed along one of these lines, it develops

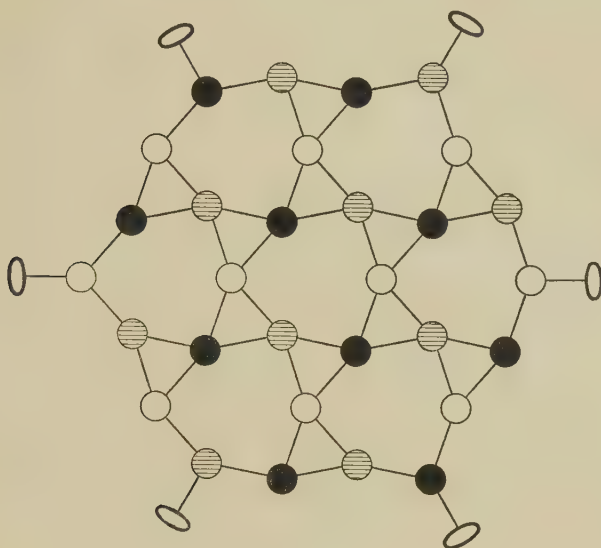


FIG. 13.

electrical charges at the opposite ends of the line, and this experimental fact is clearly reconcilable with the want of symmetry shown in the figure.

We now proceed to consider to what extent the structure arrived at can explain the physical properties of quartz; and, first, we may take the remarkable twinning effects, of which no less than four varieties are exhibited by α quartz. In the first of these (Miers, 'Mineralogy,' p. 370) a right- (*or* left-) handed crystal is twinned so that various parts of a crystal of the usual form (hexagonal prism capped by hexagonal pyramids) belong to one or other of two styles, differing in the sense of the electric axes. Alternatively stated, the structure of one style can be derived from that of the other by a rotation of 180° about the crystal axis. The two styles are related to one another in the same way as fig. 13 to its rotation through 180° in its own plane.

In the second and third varieties of twinning, right-handed portions are joined to left-handed portions so as to have the same principal axis. In the fourth variety twinning takes place across a plane passing through a pyramid edge and making equal angles with the faces on either side of the edge; this produces the curious effect in which two quartz crystals of ordinary appearance are joined together nearly at right angles. Such crystals have been found in France and in Japan.

When the temperature of α quartz crystals is raised to the critical point, such differences disappear as depend on the difference between the two styles mentioned in relation to fig. 13. The first variety of twinning disappears altogether, the second and third varieties become united into one; the fourth remains. It is simpler, therefore, to consider the twinings of β quartz before those of α quartz.

A twinning plane must have special characteristics. It must be a strong plane, containing a dense packing of atoms; for this is not only reasonable, but in agreement with all cases hitherto examined. It must be such that if the crystal is built up to this plane, its continuance on the other side of the plane may follow one or two (or more) alternatives. One of the latter is correct and continues the plan; the other must not be quite so easy to follow, otherwise there would be no regularity of structure at all.

If we take a section of β quartz, either normal to the principal axis, or to any of the digonal axes, so as to pass, say, through silicon atoms, the arrangement of the atoms in the plane is quite symmetrical. For instance, the arrangement in a plane parallel to a prism face is as shown in fig. 14 where the full

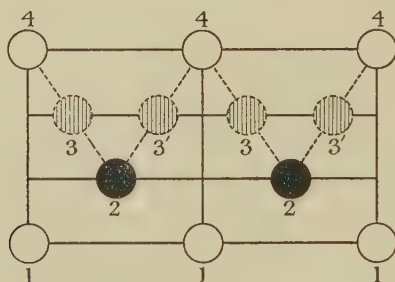


FIG. 14.

circles (1, 1, 1 ... 2, 2, 2 ... and 4, 4, 4) represent the silicon atoms in the plane. There is no difference as regards these atoms between the top and bottom, or between the two sides of this figure. It is only when we take into account silicon atoms in a neighbouring layer, denoted by 3 3 3, 3' 3' 3', that the absence of symmetry becomes clear, and the spiral character appears. The nearest silicon atoms below the paper are shown as dotted circles, and may lie either as at 3, 3, 3 ... or 3', 3', 3' The sequence 1 2 3 4 gives a right-handed spiral; the sequence 1 2 3' 4 a left-handed spiral.

If we suppose the structure to have been completed up to the level of the paper, with the silicons just below this level in the positions 3, 3, 3, &c., then the silicons just above the paper must lie in the 3', 3', 3' positions if the right-

handed arrangement is to be continued. But if the silicons just above the paper lie as at 3, 3, 3, ... , directly over those that are behind, then a new arrangement is begun, which is left-handed. If it is continued as begun, a left-handed and a right-handed crystal are twinned across the plane of the diagram, the plane in which the arrangement of silicons is the same for both. The silicons lying in the plane are in somewhat different case to the other silicons of the structure, since the oxygen atoms cannot be ranged round them in a regular tetrahedron; and we may suppose that it is just this which prevents the irregularity from being of frequent occurrence.

Similar conditions hold also in respect to the plane perpendicular to a prism face, and the plane perpendicular to the principal axis; for the sake of brevity we do not go into these in detail.

We must not affirm that whenever a crystal plane has symmetry, as in these cases, the crystal can twin about the plane. The possibility of twinning must depend on the extent of the influence which is exerted by atoms just out of the plane. It might have been that, in the case we have been considering, the influence of the silicons marked 3, 3, 3 ... (fig. 14) could have entirely prevented the silicons in the plane just above the paper from going into the wrong places; possibly through the resistance to distortion of the bonds about the silicon atoms in the plane. In that case there would have been no twinning. We are assuming that the influence is now and then insufficient to prevent twinning.

Now, if twinning can take place across any of three planes at right angles to each other, the twin forms can fit with each other in any way; and this may be taken to be the explanation not only of the twinning but also of its interpenetrant character; so that the crystal of ordinary form displays the characteristics of both kinds at various points of its surface.

The other form of twinning which β quartz may display takes place across a plane passing symmetrically through a pyramid edge. It seems to be reasonably explained in the following way.

A section of the crystal parallel to the twinning plane shows the arrangement of fig. 15, in which A, B, C are silicon atoms, D, E are oxygens. The section and the atoms mentioned belong to the upright prism in the figure. The A, D and E atoms lie in the section, B lies a little above it, C a little below. The lengths of the perpendiculars from B and C upon the plane of section are each 0.30 A.U. nearly. The upright prism of the figure is right-handed, if we so denote the structure which has a right-handed spiral round the triangle of figs. 10, 12, or 13, and therefore a left-handed spiral round the hexagon of the same figures.

If B and C are shifted to the left side of the section the crystal becomes left-handed. Now if we take such a left-handed block, it will not, of course, fit

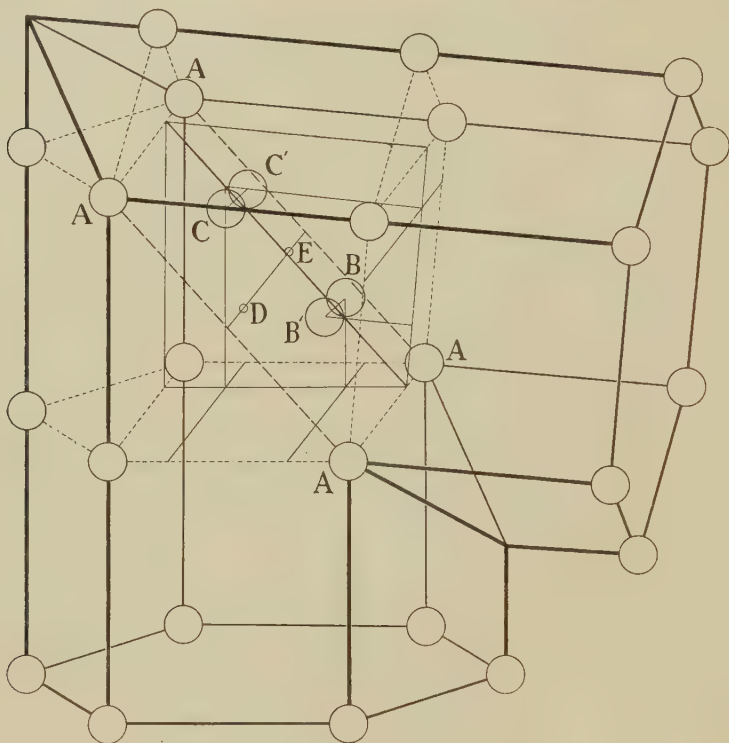


FIG. 15.

on to the block in fig. 15 so as to continue the prism, but it will, with a little strain, fit on as shown in the same figure. The atoms at B and C will be forced into the plane of section, in other words B'C' belonging to the upper block will coalesce with B, C belonging to the lower. The necessity for the strain so caused will prevent the effect being more than very occasional. This explanation requires that one of two portions having the sectional plane in common shall be right-handed and the other left. There is no possibility, unfortunately, of testing the hypothesis by the examination of the twinned crystals; in all known cases both portions are mixtures of right and left. At least, however, there is nothing against the explanation suggested.

It is now easy to complete the list of twinings of α quartz. Right-handed β quartz may, as we have seen, be combined with left-handed, so as to form interpenetrating portions of a crystal having as a whole the hexagonal prismatic form. If the quartz is allowed to cool and form α quartz, the right-handed and

the left-handed portions may develop their electric axes either in the same sense or in opposite senses. In either case there is a plane of symmetry, since the right is the reflection of the left. If the electric axes have the same sense, the planes of symmetry must contain the axes, that is to say, must pass through the prism edges. This (Miers, p. 371, case 3) is the rarer form. If the electric axes in the two portions are in opposite senses, the plane across which one portion reflects into the other must be perpendicular to an electric axis. This gives the commoner form, known as the Brazil twin.

Lastly we have the case first mentioned, in which a right-handed or left-handed crystal is divided into portions—it may be quite irregularly—which display opposite polarities along their electric axis; or in other words can be brought to structural coincidence by a 180° rotation of one kind with respect to the other round the principal axis. When a right-handed β crystal cools down, it may well happen that different portions develop the opposite polarities; and if the consequent strain does not break up the crystal, we have the twinning under consideration. It is said that this effect is of frequent occurrence: yet the strain is apt to cause fracture. If we look into the structure to see how its arrangement permits such twinning, we find that as in the other cases the two opposite structures have a number of planes in which the arrangement of the atoms is exactly the same for the two cases; so that in each case a plane might be used as a foundation for either structure, were it not for the secondary influence of atoms in the neighbourhood of the planes.

We may next consider the piezo-electrical and pyro-electrical properties. These properties are developed in a direction at right angles to the principal axis; so that we may consider them with reference to fig. 13, which shows the positions of the atoms as projected on the principal plane. It will be observed that the figure may be regarded as an aggregate of triangles, each of which has a silicon atom at each corner; there is also, though it is not shown in this figure, an oxygen atom close to the middle point of each edge. The existence of pyro- and piezo-effects shows that there must be a separation of electric charges between the two kinds of atoms. It is at least permissible to assume that each silicon has a positive charge of 4, and each oxygen a negative charge of -2 . Each triangle may be considered to have an equal share in three silicons, and to possess three oxygen atoms entirely. Thus the unit of the figure may be represented as in fig. 16.

The electric field due to such an arrangement of charges is extremely weak at great distances, since the symmetry is so great: close to the triangle the field is stronger and is trigonal in form. In β quartz the triangles are of exactly

opposed orientations, and in consequence the external field due to the whole arrangement is entirely negligible.

If the crystal cools down to the α form the two kinds of triangle rotate in

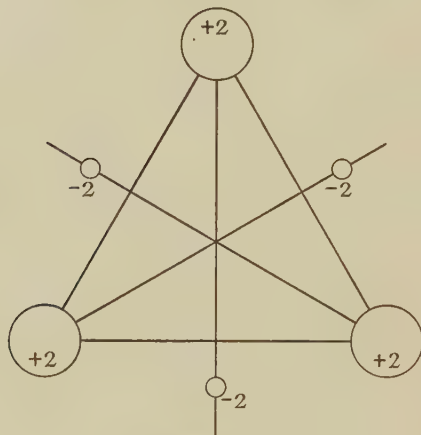


FIG. 16.

opposite senses, and no longer compensate each other: thus a trigonal electric field exists. The intensity of the field will vary with the amount of rotation, and therefore with temperature; and if it is compensated by any means at a certain temperature, a change of temperature will give rise to charges, the orientation of which will depend on the sign of the change. It seems likely that change of temperature will act by causing the triangles to rotate; there seems no reason for supposing the triangle to change in form.

On the other hand, pressure along an electric axis must cause distortion in the triangle. If it merely caused rotation—and it might well cause *some* rotation—then the results of pressure along one electric axis would be the production of equal charges along all three axes. Pressures on all three axes would be cumulative in their effects. But experiment shows that uniform pressure produces no electrification, and we conclude that piezo-electricity is due to distortion of the triangle.

The electrical conductivity of quartz has been the subject of much measurement. Nearly forty years ago Jacques and Pierre Curie devised a method, which has been used by Röntgen, S. W. Richardson and Joffé.

The general results are very striking. The conductivity is very low, of course. It is hundreds of times greater along than across the axis, it increases very rapidly with temperature and it presents strong analogies with the conductivity

of a gas. Joffé, in a paper presented to the Solvay Congress of Physics in 1924, stated that the conductivity could be expressed in the form

$$\sigma = Be^{A/T},$$

where A is the same for quartz in both directions, for Iceland spar, for ammonium alum, and other crystals. The value of A is -1.15×10^4 .

The form of the expression suggests—as Joffé points out—that the current is carried by ions. The constant B , independent of temperature, will represent the whole number of ions available. This will depend not only on how many ions there are in the crystal, but on how many can traverse it; and this will depend on the direction in the crystal. The exponential suggests that the motion of the ions follows the gaseous laws, and that since the value of A is so high, only the fastest take part in the conduction. In fact, the value of A is not very different from the corresponding constant in O. W. Richardson's thermionic equation, which is about -5×10^4 . It makes little difference that the thermionic expression contains a factor $\sqrt{T}$ while Joffé's does not.

The structure we have found is far from suggesting, in itself, the explanation of all these appearances; but it is probably of some consequence that the structure possesses more open and more direct passages along than across the axis, that the size of the passages is of the right order to allow ions to go along them, and that the difference between the sizes along and across the axis is such that one may reasonably suppose the lithium and sodium ions to be able to move one way, but only the lithium ions the other. In general, the structure is compatible, so far as can be seen, with Joffé's theory of the conductivity of quartz.

The actual values of the changes in the positions of the atoms which occur when β is transformed into α quartz have been calculated by one of us (R. E. Gibbs) and form the subject of a separate paper.

We desire to acknowledge gratefully the assistance given by the Department of Scientific and Industrial Research. We have also to thank Prof. Gordon for his help in preparing specimens.

*The Light of the Night Sky: its Intensity Variations when
Analysed by Colour Filters.—II.*

By LORD RAYLEIGH, F.R.S.

(Received August 7, 1925.)

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§1. *Introduction.*

THE present paper describes a further instalment of the work initiated in 'Roy. Soc. Proc.,' A, vol. 106, p. 117, 1924. Although the ultimate outcome of the whole investigation is far from being apparent as yet, some of the methods have been improved, and data accumulated which make it possible to be more definite on certain points. Since the scheme of observation has been in the main the work of one individual, both in conception and execution, it is important to place the results on record from time to time, to prevent any risk of their being lost.

It will be remembered that the light of the night sky was passed through a colour filter, and the intensity matched against a permanent self-luminous (radioactive) source, using neutral glasses of known opacity to reduce the two to equality. The filters used were three in number :—

- (a) Wratten 23A, orange, not transmitting the light of the green aurora line λ 5578.
- (b) Wratten 21, combined with dense didymium glass.* This is designed to isolate λ 5578 as nearly as possible.
- (c) Wratten 65A, greenish blue, excluding λ 5578, but transmitting freely above this limit.

* Since writing the former paper I have learned that this is a soda glass containing 10 per cent. of crude didymium oxide. As mentioned before, it was made for Sir William Crookes.

In addition to the comparisons with the self-luminous standard, direct comparisons were made between (*e.g.*) the blue and orange components of the light of the night sky. For details of the methods, the former paper must be consulted.

I gave reasons for thinking that the line 5578 seen in the night sky in temperate latitudes is excited by a different agency from that which acts in the polar regions, and proposed for it the name non-polar aurora.

§2. *Use of Photoelectric Cell for Measuring Opacities of Neutral Glasses.*

In the former experiments the neutrality of the opaque glasses was relied on, *i.e.*, they were considered to have the same opacity whichever colour filter they were used with. The opacities were determined by a sector photometer, using the light of an incandescent lamp.

This procedure has now been improved upon by using a photoelectric cell for determining the opacity. The arrangement is the same as that formerly used for measuring the opacities of photographic plates.* The light of a pointolite lamp is approximately focussed on the "neutral" glass, and then traverses a colour filter, finally entering a photoelectric cell. The potassium cells formerly used for this purpose are useless for green, yellow or red light, and a vacuous rubidium cell was substituted.† The current through the cell was read by the direct deflection of a high-resistance galvanometer, and the opacity was determined by observing the proportional increase of this deflection when the neutral glass was removed. Using this method with care, and avoiding deflections large enough to cause a shift of the zero, the opacity could be determined within 1 per cent. This is more than enough for the purpose, and it was not thought worth while to work out a more accurate null method, though this could doubtless be done. The opacities of the glasses for the various colours used in the actual observation were thus determined, and in the case of some of the denser glasses were found to differ appreciably from the older visual values. All the old results have been recalculated on this basis, and the corrected values are here given. The corrections are, however, in most cases unimportant, and do not in any way affect the general conclusions of this or the former paper. The spontaneous light of the uranium salt itself is taken to be of a green tint, like its fluorescence in sunlight, and when a "neutral" glass is used to reduce it the opacity value for green light is used. The method reveals an appreciable

* 'Roy. Soc. Proc.,' A, vol. 97, p. 441 (1920).

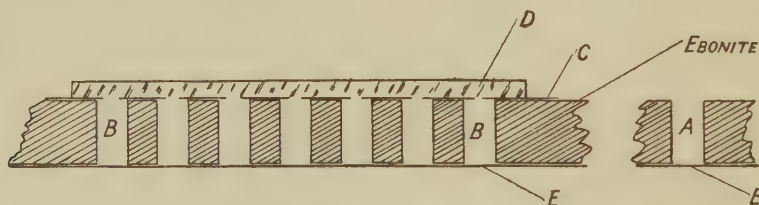
† It was supplied by the research laboratory of the General Electric Co., Wembley, Middlesex.

defect of neutrality in some of the more opaque of the "neutral" glasses used.

§3. *Photographic Intensities.*

In addition to the observations with the three colour filters, the shorter wave-lengths present in the night sky have on many occasions been registered photographically. The photographic region of the spectrum may be considered as centred at about $\lambda 4300$, and its more intense part extends from about $\lambda 3900$ to $\lambda 4600$. The green auroral line has no appreciable action on the (ordinary) plates used.

In order to get a scale of intensities a sensitometer arrangement was used, consisting of a series of pinholes of graduated size, separated from the plate by a little distance, and backed by an opal glass. This was exposed to a standard candle at 5 feet distance for 15 minutes, and then an exposure was made to the sky for the same interval. The sky exposures were made with an aperture of $\frac{1}{8}$ inch at a distance of $\frac{1}{4}$ inch from the plate. A series of such apertures was arranged beside the standard scale already mentioned. The intensities of the sky exposures (which were all the same except for inequalities in the photographic plate) were compared with those of the standard scale by means of the photo-electric cell as already described at the fraction of an interval interpolated. The values of the scale divisions were calculated from the relative areas of the pinholes, as measured under a travelling microscope. In constructing the arrangement each hole was made as nearly as possible 1.26 times the area of its predecessor, so that the logarithm should increase by 0.1. But in practice this was not well attained, and the measured value was used, the scale being thus slightly irregular. Seven holes were provided, giving a range of about 1 to 5 (see figure).



A. Plain hole in ebonite, as used for sky exposure. BB. Series of holes for candle light exposure. C. Copper foil, with series of graduated apertures. D. Diffusing layer of opal glass. EE. Photographic plate.

There are two rows of the plain holes A, one on each side of the row B. The A series and the B series have independent covering slides.

It was found convenient to expose several plates to the standard candle, so as to impress the standard scale, and to store them ready for the night work.

Each plate was developed immediately after the sky exposure. In the later part of the work two exposures were usually made on the same night if opportunity offered. They did not always agree as well as might be wished, and, generally, the method is not regarded as satisfactory or final. The standard candle is not a sufficiently constant source of light. Moreover, there was a risk of the plate being affected by the deposition of dew.

A modified method is being developed, in which the exposure to the sky and to the standard light will be simultaneous. It is thought that this will much facilitate the routine work, as the precise length of exposure will be immaterial.

§4. Tabulated Results of the Measurements.

The tables have been given to three significant figures. This is done with hesitation, as in nearly all cases two would be quite enough. Possibly, however, a little accuracy might be sacrificed in a few cases if the third were not given. It must be remembered that these three figures represent the determined value of a neutral glass, which gave a match. The three are required to represent the accuracy of this determination, though two would nearly always represent the accuracy with which the sky component can be equated to it.

The auroral values up to and including October 29, 1923, were made with a different instrument, and different neutral glasses, to those which follow. They have been reduced to the same scale by applying the factor 0.614, which has been determined by the "artificial sky" method presently to be referred to. This factor is much more accurate than the factor 0.54 used in the former paper, which was determined by parallel observations on the actual sky—a far less satisfactory method. The opacity of the neutral glasses used has been redetermined by the rubidium cell as in the other case.

Date.	Red.	Aurora.	Blue.	Photographic.		Date.	Red.	Aurora.	Blue.	Photographic.	
				I.	II.					I.	II.
1923.						1923.					
Feb. 16	—	0.508	—	—	—	May 3	—	0.318	—	—	—
Feb. 17	—	0.508	—	—	—	May 4	—	0.318	—	—	—
						May 5	—	0.318	—	—	—
Mar. 5	—	0.614	—	—	—	May 18	—	0.318	—	—	—
April 4	—	0.318	—	—	—	July 20	—	0.376	—	—	—
April 7	—	0.318	—	—	—						
April 8	—	0.318	—	—	—	Aug. 2	—	0.614	—	—	—
April 10	—	0.376	—	—	—	Aug. 3	—	0.614	—	—	—
April 13	—	0.376	—	—	—	Aug. 4	—	0.614	—	—	—
April 14	—	0.376	—	—	—	Aug. 5	—	0.614	—	—	—
April 17	—	0.376	—	—	—	Aug. 6	—	0.614	—	—	—

Date.	Red.	Aurora.	Blue.	Photographic.		Date.	Red.	Aurora.	Blue.	Photographic.	
				I.	II.					I.	II.
1923.						1924.					
Aug. 7	—	0·614	—	—	—	Jan. 25	0·228	0·315	1·19	1·55	—
Aug. 8	—	0·614	—	—	—	Jan. 27	0·262	0·427	1·19	2·33	—
Aug. 9	—	0·614	—	—	—	Feb. 1	0·165	0·351	1·55	—	—
Aug. 11	—	0·614	—	—	—	Feb. 28	0·255	0·493	1·19	—	—
Aug. 13	—	0·614	—	—	—	Mar. 1	0·228	0·427	1·19	2·11	—
Aug. 15	—	0·614	—	—	—	Mar. 4	0·262	0·493	1·55	—	—
Aug. 17	—	0·614	—	—	—	Mar. 5	0·262	0·645	1·19	3·02	3·09
Aug. 31	—	0·614	—	—	—	Mar. 6	0·262	0·645	1·55	3·67	3·16
Sept. 2	—	0·614	—	—	—	Mar. 8	0·228	0·493	1·55	2·32	—
Sept. 4	—	0·614	—	—	—	Mar. 9	0·228	0·493	1·55	2·26	—
Sept. 7	—	0·614	—	—	—	Mar. 10	0·228	0·565	1·55	2·00	—
Sept. 8	—	0·483	—	—	—	Mar. 24	—	0·565	—	—	—
Sept. 9	—	0·483	—	—	—	Mar. 29	0·255	0·645	1·77	—	—
Sept. 15	—	0·483	—	—	—	Mar. 30	0·255	0·645	1·77	2·72	—
Sept. 16	—	0·614	—	—	—	Mar. 31	0·255	0·565	1·77	2·16	—
Sept. 18	—	0·614	—	—	—	April 1	0·255	0·493	1·77	1·65	2·00
Sept. 30	—	0·614	—	—	—	April 4	0·255	0·565	1·77	2·38	—
Oct. 1	—	0·614	—	—	—	April 5	0·255	0·493	1·77	1·65	—
Oct. 3	—	0·614	—	—	—	April 6	0·255	0·493	1·55	1·62	—
Oct. 5	—	0·614	—	—	—	April 7	0·255	0·565	1·55	1·69	—
Oct. 7	—	0·614	—	—	—	April 8	0·315	0·645	1·77	—	—
Oct. 9	—	0·483	—	—	—	April 25	0·262	0·427	1·55	—	—
Oct. 12	—	1·00	—	—	—	April 27	0·255	0·427	2·03	1·80	—
Oct. 13	—	1·00	—	—	—	April 30	0·255	0·427	2·03	—	—
Oct. 14	—	0·614	—	—	—	May 2	0·255	0·427	1·55	—	—
Oct. 15	—	0·614	—	—	—	May 5	0·255	0·493	2·34	1·90	—
Oct. 16	—	0·614	—	—	—	May 7	0·255	0·493	2·03	—	—
Oct. 29	—	1·00	—	—	—	July 29	0·315	0·840	2·34	1·42	—
Oct. 31	0·493	1·00	1·55	—	—	July 30	0·255	0·565	2·34	—	—
Nov. 2	0·351	0·493	1·55	—	—	Aug. 2	0·255	0·645	2·34	—	—
Nov. 3	0·351	0·493	1·55	—	—	Aug. 5	0·315	1·00	2·34	1·42	—
Nov. 4	0·255	0·493	1·19	—	—	Aug. 7	—	0·840	1·77	2·11	—
Nov. 6	0·255	0·493	1·00	—	—	Aug. 27	0·262	0·645	1·77	—	—
Nov. 7	0·255	0·427	1·00	—	—	Aug. 31	—	0·840	—	—	—
Nov. 10	0·255	0·427	1·19	—	—	Sept. 1	0·255	0·645	2·03	—	—
Nov. 11	0·255	0·565	1·19	—	—	Sept. 3	0·262	0·565	1·77	—	—
Nov. 14	0·255	0·565	1·19	—	—	Sept. 17	—	1·00	—	—	—
Nov. 15	0·255	0·565	1·55	—	—	Sept. 21	0·255	0·840	2·03	—	—
Nov. 30	0·214	0·315	1·00	—	—	Sept. 22	—	1·00	—	—	—
Dec. 2	0·214	0·315	1·19	—	—	Sept. 24	0·351	1·00	2·34	—	—
Dec. 3	0·165	0·255	0·840	—	—	Sept. 25	0·255	0·645	1·55	—	—
Dec. 4	0·139	0·255	1·00	—	—	Sept. 26	0·255	0·645	1·77	—	—
Dec. 6	0·139	0·255	1·19	—	—	Sept. 27	0·255	0·645	1·77	—	—
Dec. 8	0·165	0·255	1·19	—	—	Sept. 29	0·351	0·565	1·77	—	—
1924.						Sept. 30	—	0·645	—	—	—
Jan. 2	0·255	0·351	1·55	—	—	Oct. 1	0·351	0·565	1·77	—	—
Jan. 3	0·165	0·255	1·00	—	—	Oct. 17	0·427	0·645	1·55	—	—
Jan. 4	0·228	0·315	1·19	1·72	—	Oct. 22	0·427	1·19	2·03	2·33	—
Jan. 5	0·165	0·255	1·19	1·55	—	Oct. 23	0·427	1·00	2·03	2·11	—
Jan. 6	0·165	0·255	1·00	1·69	1·83	Oct. 24	0·427	1·00	2·34	3·17	—
Jan. 7	0·165	0·255	1·00	1·42	—						
Jan. 12	0·165	0·315	1·55	—	—						

Date.	Red.	Aurora.	Blue.	Photographic.		Date.	Red.	Aurora.	Blue.	Photographic.	
				I.	II.					I.	II.
1924.						1925.					
Oct. 25	0.493	1.19	3.18	2.72	—	Jan. 28	0.255	0.427	1.55	1.42	1.71
Oct. 28	0.493	1.00	1.77	1.92	2.11						
Oct. 30	0.427	0.645	1.55	1.39	1.62	Feb. 12	0.255	0.645	1.77	—	—
Nov. 2	0.351	0.645	1.55	1.94	—	Feb. 14	0.255	0.840	2.03	3.24	—
Nov. 3	0.427	0.645	1.55	2.49	2.57	Feb. 17	0.255	0.493	1.77	2.11	2.22
						Feb. 18	0.255	0.427	1.55	1.51	1.90
Nov. 15	0.427	0.565	1.55	2.38	2.33	Feb. 19	0.255	0.351	1.55	1.69	1.80
Nov. 17	0.427	0.427	1.55	1.83	1.94	Feb. 20	0.255	0.427	1.55	2.00	2.16
Nov. 19	0.315	0.351	1.00	—	—	Feb. 21	0.255	0.351	2.03	2.22	2.11
Nov. 20	0.351	0.427	1.55	1.40	1.48	Feb. 22	0.255	0.427	2.03	2.16	—
Nov. 25	0.351	0.427	1.55	1.87	1.80	Feb. 24	0.255	0.565	1.55	2.11	2.11
Nov. 27	0.262	0.351	1.19	1.55	1.52						
Nov. 28	0.262	0.427	1.77	1.45	2.05	Mar. 12	0.255	0.565	1.77	2.22	—
						Mar. 15	0.255	0.645	1.77	—	—
Dec. 17	0.351	0.565	1.55	1.45	1.72	Mar. 17	0.255	0.565	1.77	2.11	1.80
Dec. 18	0.351	0.565	1.55	—	—	Mar. 18	0.255	0.565	1.55	1.87	2.16
Dec. 19	0.255	0.427	1.55	2.00	2.03	Mar. 21	0.255	0.565	1.55	2.22	—
Dec. 22	0.351	0.565	1.55	2.27	2.22	Mar. 22	0.255	0.565	1.55	2.33	2.22
Dec. 24	0.351	0.493	1.77	2.11	2.27	Mar. 23	0.255	0.565	1.55	2.11	—
Dec. 25	0.351	0.493	1.77	1.76	2.11	Mar. 25	0.255	0.565	1.55	1.65	1.39
Dec. 26	0.427	0.645	1.77	2.57	2.16	Mar. 27	0.255	0.565	1.55	1.69	1.94
Dec. 28	0.427	0.840	1.77	2.33	2.33	Mar. 28	0.255	0.565	1.55	—	—
Dec. 29	0.315	0.565	1.77	—	—						
Dec. 30	0.315	0.565	1.77	1.80	2.22	April 12	0.262	0.427	1.55	1.36	—
Dec. 31	0.255	0.565	1.77	—	—	April 13	0.262	0.427	1.55	—	—
						April 15	0.315	0.565	2.03	1.83	2.00
1925.						April 17	0.255	0.493	1.55	—	—
Jan. 18	0.315	0.565	1.77	2.49	2.27	April 21	0.255	0.493	2.03	2.16	—
Jan. 22	0.255	0.427	1.55	1.90	2.05	April 23	0.255	0.493	2.03	2.05	—
Jan. 23	0.315	0.493	1.77	2.33	2.05	April 24	0.255	0.427	1.77	1.52	—
Jan. 24	0.255	0.351	1.55	1.69	1.45	April 26	0.228	0.351	1.77	—	—

§5. *Comparative Intensities for the Various Components.*

As in the former work, the intensities of the various components have been compared directly with one another, without reference to the standard self-luminous source. To save space, these observations have not been given in detail, but it has been thought worth while to select the extreme cases of variation, and to exhibit them in comparison with the entirely independent value obtained by comparison of each component separately with the self-luminous source. The latter method is, of course, subject to the cumulative error of two photometric comparisons.

Blue/Aurora.

Date.	Aurora.	Blue.	Blue/Aurora calculated.	Blue/Aurora observations.
1924—April 27	0.427	2.03	4.8	4.4
1925—April 24	0.427	1.77	4.1	4.4
1924—May 5	0.493	2.34	4.7	4.4
1924—October 28	1.00	1.77	1.8	2.0
1924—October 22	1.19	2.03	1.7	2.0

Red/Aurora.

Date.	Aurora.	Red.	Red/Aurora calculated.	Red/Aurora observations.
1924—November 17	0.427	0.427	1.0	1.0
1924—November 15	0.565	0.427	0.76	0.84
1924—August 5	1.0	0.315	0.32	0.26
1924—July 30	0.565	0.255	0.45	0.26

Blue/Red.

Date.	Blue.	Red.	Blue/Red calculated.	Blue/Red observations.
1923—October 31	1.55	0.493	3.1	2.8
1924—October 30	1.55	0.427	3.6	3.9
1924—November 15	1.55	0.427	3.6	3.9
1924—November 17	1.55	0.427	3.6	3.9
1924—May 5	2.34	0.255	9.1	8.4
1924—July 29	2.34	0.315	7.4	8.4
1924—July 30	2.34	0.255	9.2	8.4
1924—August 5	2.34	0.315	7.4	8.4
1924—September 3	1.77	0.262	6.8	8.4

The agreement between the direct comparisons and those calculated by eliminating the standard light is on the whole not unsatisfactory. The present work amply confirms that of last year in showing that the light of the night sky is subject to variations of quality as well as quantity.

It is to be remarked that this seems to dispose of any uncertainty that might remain about the results being seriously vitiated by varying atmospheric transparency. Very marked variations, not only in the density but also in the selective absorbing power of the atmospheric veil, would have to be assumed in order to explain the results away.

It is not easy to assume a dense atmospheric veil at all on starlight nights, on which alone observations were recorded. If, however, there is such a veil, then, according to all experience, it would transmit red light better than

blue. If we try to explain the cases where red light is relatively preponderant (*e.g.*, October 31, 1923) by postulating an exceptionally dense veil, we encounter the difficulty that the blue light is not appreciably below its average for all clear nights, while the red is appreciably above its average.

Obviously such a veil would be worse than useless as an explanation of the cases where the blue light is preponderant. Can we, then, postulate a veil selectively transmitting blue? Such a supposition would be purely *ad hoc* and unsupported by any other known phenomenon. Moreover, it would not be of any real help, for when blue light is preponderant (*cf.* July 29, 1924) this component is above the average for all clear nights, while the red component is not appreciably, if at all, below the average. A blue transmitting veil could not enhance the blue component. At the best it could only leave it unaltered.

§6. *Correlation between the Various Components.*

As we have seen, the intensity ratios of the different components of the light vary considerably. Are these components, then, completely independent?

Last year the available data were too few for satisfactory discussion, but they are now more adequate.

It has not been thought worth while to print the complete correlation tables showing the connection of the auroral light with the other components; they can, of course, be re-compiled from the data already given. In the following table the first column gives the successive intensities of auroral light according to the rather irregular scale used,* and the remaining columns give the mean values of the other components corresponding to the value of the auroral light in the first column.

Auroral.	Mean of Red.	Mean of Blue.	Mean of Photographic.
0.255	0.158	1.05	1.58
0.315	0.210	1.22	1.64
0.351	0.249	1.52	1.76
0.427	0.272	1.56	1.81
0.493	0.274	1.65	2.02
0.565	0.284	1.65	2.08
0.645	0.303	1.71	2.51
0.840	0.332	2.05	2.28
1.00	0.418	2.06	2.18
1.19	0.460	2.60	2.52

* The scale proceeds by somewhat irregular steps because the neutral glasses used were those at hand, and it was not at that time thought worth while to go to the trouble of preparing a series increasing by uniform steps. Having once started work with this irregular scale, there were obvious objections to changing it.

It will be evident at a glance that the red and blue components are highly correlated with the auroral component. The photographic component is also correlated, though less highly, the values for the mean showing some irregularity of order. This is partially explicable by the small number of photographic observations, which were only 71 in number, compared with 119 in the other cases. But the amount of correlation is actually less, as well as being less accurately fixed.

Coming to the actual coefficients, by which the correlation is measured, these were calculated by the usual formula

$$\frac{\Sigma xy}{\sqrt{\Sigma x^2 \Sigma y^2}}$$

where x and y are the deviation of corresponding values from the mean.

The values, with their probable errors, are :—

Aurora—red	0·70 ± 0·03
Aurora—blue.....	0·66 ± 0·04
Aurora—photographic.....	0·44 ± 0·06

The aurora-photographic correlation is noteworthy, because the photographic region of the spectrum (for the ordinary plates, without colour sensitiveness, which were used) is far removed from the aurora line, and because the experimental methods used in measuring the photographic intensities were such as to eliminate all possibility of bias. These latter were all measured in a series at the end of the work, and without having the visual results for the corresponding dates at all in mind.

§7. *Variations of the Total Light.*

In addition to the measurement of the various components, the general light of the sky, reduced with a neutral glass, has been compared with the standard.

This cannot tell us any more about the course of the variations than can be learnt by considering individual chromatic components. Nevertheless, it is of interest for comparison with the results of other observers who have limited themselves to the consideration of the total light.

I give only the exceptionally high and exceptionally low values, with the two more important individual components, auroral and blue, for comparison.

Date.	Total Visual Light. Arbitrary Scale.	Auroral Light. Arbitrary Scale.	Blue Light Arbitrary Scale.
1923—December 4	3.4	0.26	1.00
1924—January 3	3.4	0.26	1.00
1924—July 29	8.4	0.84	2.34
1924—August 2	8.4	0.65	2.34
1924—August 5	8.4	1.00	2.34
1924—September 24.. ..	10.0	1.00	2.34
1924—October 25	10.0	1.19	3.18

As should be the case, the first two of these values are on nights when the blue and auroral components are both exceptionally low, and the five last on nights when both these components are exceptionally high.

It is of interest to remark that the highest value yet encountered—that of October 25, 1924—occurred on a night noted as “not very clear.” Here, again, we see how changeable transparency of the atmosphere fails to afford any sufficient explanation of the observed variations.

§8. Search for Connection with other Variable Quantities.

It was desirable to compare the auroral intensity with other variables in cosmical or terrestrial physics. In this section I have used only the values after October 30, 1923.

Sunspot Area.—The projected areas in millionths of the sun’s visible disc were kindly supplied by the Astronomer Royal. The mean is tabulated below for each value of the auroral intensity.

Magnetic Disturbance.—Here, again, the data were kindly supplied by the Astronomer Royal, the degree of disturbance being estimated by the character figure 0, 1, or 2. The mean figure is tabulated against the auroral intensity in column 3.

Barometric Height.—This is tabulated against the auroral intensity. The readings were taken off the charts of a barograph in domestic use.

Auroral Intensity.	Mean Spot Area.	Mean Magnetic Character.	Barometric Heights, 29 inches +
0.255	0	0.375	0.80
0.315	0	0.400	0.96
0.351	424	0.500	0.85
0.427	460	0.195	0.72
0.493	189	0.500	0.78
0.565	299	0.267	0.84
0.645	397	0.526	0.70
0.840	865	0.167	0.55
1.00	501	0.875	0.88
1.19	401	0.500	0.80

I have not thought that there was enough indication of correlation in any of these cases to make it worth while to compute the coefficient. It would almost certainly be found to have a probable error so large as to deprive it of all significance.

The spot area and the magnetic character have not much statistical regularity, with the number of observing days available for discussion. In the case of spot area, this is due to the great inequalities introduced by the appearance of individual spots when spots are few, as they have been during the whole relevant time.

Similarly, in the case of magnetic character figure, the number 0 appears in a considerable majority of all cases, and an exceptional amount of disturbance, denoted by 2, consequently introduces great inequalities.

To lessen the effect of these irregularities, we may divide the whole series of nights into two approximately equal numbers, according to whether the auroral intensity is or is not above 0.493. We then get :—

Auroral Intensity.	Mean Spot Area.	Mean Magnetic Character.	Mean Barometric Height Inches.
0.493 or less.....	265	0.37	29.78
Above 0.493.....	402	0.42	29.77

There is no suspicion of any connection, except possibly in the case of the spot area. It must be remembered that the spot area on any given day is a very vague indication of the phase of the solar cycle, which only comes out statistically from the mean spot area taken over a year, or at least an appreciable fraction of a year. When enough data are available, the connection, if any, should be discussed in this way, but the result will hardly be conclusive until a cycle is nearly completed.

§9. *Does the Intensity Vary Systematically with the Sun's Distance below the Horizon?*

The origin of the light of the non-polar aurora is unknown. If the stimulus comes from the sun, it certainly cannot come in a rectilinear path, but must in some way get round the earth's curvature. Twilight gets round by atmospheric scattering. Similarly, electric waves used in radio-telegraphy get round, it is believed, by reflexion at an overhead layer. The corpuscular rays from the sun which are invoked in the received explanation of the polar aurora get round by magnetic deflection. In this connection it is evidently important to determine the march of intensity as the sun's distance below

the horizon increases. Favourable opportunities for studying the question are not numerous in this country, as observations throughout the night can only be made at the time of new moon and in the winter, with the sky clear at nightfall.

On December 22, 1924, the changes were carefully watched as night conditions set in. It was, of course, impossible to observe quite simultaneously with the various colour filters. The quantities measured were (1) the light transmitted by the auroral filter; (2) the total intensity, using a neutral glass to reduce it to equality with the luminous standard; (3) the ratio red to blue, which, as shown formerly, increases largely as the twilight fades out. These three quantities were measured exactly as in the routine night sky work. The local time of each observation was noted.

Local Time, p.m.	Total Intensity.	Auroral Intensity (Apparent.)	Ratio Red/Blue.
5.18	—	1.77	—
5.23	—	—	0.0746
5.25	—	1.0	—
5.29	13.4	—	—
5.34	—	—	0.139
5.35	—	0.645	—
5.37	8.42	—	—
5.40	6.13	—	—
5.43	—	0.565	—
5.44	6.13	0.565	—
<i>circ.</i>			
6.30	4.38	0.565	0.228
10.30	—	0.565	—

It appears from these results that the time when night conditions come on is definite within a few minutes. We may put this time at 5.44 p.m. The sun was then 16.3° down,* and the auroral intensity had the same value at that time as it had at 10.30 p.m. On that night (December 22, 1924) the sky clouded up, and no further observations could be taken.

On December 25 to 26 the following observations were secured :—

Local Time.	Auroral Intensity.
5.40 p.m.	0.493
6.30 p.m.	0.493
11 p.m.	[Cloudy]
6 a.m.	0.493
6.15 a.m.	[Cloudy]

* Night conditions are usually considered to come on when the sun is 18° down, according to an estimate due, I believe, to Tycho Brahe. The last signs of daylight are of course seen low in the west, above the sun. The present observations were made towards the pole, where all traces of daylight naturally disappear sooner.

Taking these together with the former, we may conclude that no regular variation of the auroral intensity can be detected in the course of the night. As soon as the daylight has faded sufficiently to allow definite observations to be taken, the auroral intensity takes the value which prevails at midnight and until dawn. This statement refers, of course, to a possible *regular* variation in the course of the night, directly dependent on the sun's angular distance below the horizon. Irregular variations, no doubt, sometimes occur in the night, since the auroral intensity is found to have varied appreciably from one evening to the next.

I have not actually observed one of these in progress, but observations have seldom been continued for more than an hour or two on a given night. For this purpose continuous photographic registration would have great advantages. Some preliminary trials have been made in this direction, with a photographic film wrapped round a 24-hour clockwork drum. Unfortunately, the sensitiveness of orthochromatic films is not enough to enable the auroral intensity to be registered in this way, as an adequate impression on a stationary film can hardly be got in less than a three-hour exposure, even with a cone of rays of 60° angle. The total photographic intensity (blue and violet) gives an adequate photographic trace, and on one occasion I got such a trace of sensibly uniform intensity throughout the night. This line of work might well be continued at some station where nights frequently occur which are quite free from clouds. In the south of England such nights are too rare to make it worth while to pursue the matter.

§10. *Auroral Intensity in California. Comparison with England.*

As remarked in earlier papers, it appeared very probable from the observations made in California, U.S.A., by Campbell, Slipher, and Babcock, that the green aurora line is ordinarily stronger there than in England, notwithstanding that the latitude is some 17° further south. The method of using a self-luminous radioactive source as a standard of light offers great advantages for investigating this question, for instruments can be issued to various parts of the world from one centre, after comparison with a master standard, and will remain comparable with one another.

A beginning has already been made on these lines. Mr. J. H. Jeans, F.R.S., who was visiting the Mt. Wilson observatory in the autumn of 1924, kindly took with him one of the instruments, with an auroral filter and potassium-uranyl sulphate as a source of light, and placed it in the hands of Mr. H. D. Babcock, whose kind co-operation has been most valuable.

In order to reduce the results to the same scale as my own, a careful comparison of the two instruments has been made by means of what may be called an *artificial sky*. This consists of a piece of opal glass forming the end of a wooden box about 30 inches long, and illuminated by a small incandescent lamp at the other end of the box. Care is taken that the opal is uniformly illuminated. The instrument under test is placed in a standard position, and the brightness of the artificial sky adjusted by a resistance in the lamp circuit until equality is obtained. The voltage at the terminals of the lamp is then recorded by an assistant, who reads the voltmeter in an adjoining room, when light can be freely used for the purpose. This is repeated for each instrument. The brighter of the two instruments under comparison is then reduced by a neutral glass of known opacity until it is below the other, and the observation repeated. We have then the data for comparing the brightnesses by interpolation. Fifty observations are made in each case, to eliminate the rather large random errors of the photometric settings. This preliminary explanation of the method will suffice here. A more detailed account will be given in a future paper. The instrument was handed back to me by Mr. Babcock in July, 1925, and the comparison then made. The values of the neutral glasses supplied to Mr. Babcock were checked with the photoelectric cell, and thus his observations could be reduced to the same scale as my own with satisfactory accuracy. These reduced values are given in the following table:—

Date.	Aurora.	Date.	Aurora.	Date.	Aurora.	Date.	Aurora.
1924.		1924.		1924.		1925.	
Sept. 17	1.41	Oct. 30	1.07	Dec. 28	1.00	Feb. 20	1.24
Sept. 20	1.41			Dec. 31	1.07	Feb. 24	1.24
Sept. 21	1.41	Nov. 1	1.41			Feb. 25	1.24
Sept. 22	1.07	Nov. 15	2.27			Feb. 26	1.07
Sept. 23	1.41	Nov. 16	1.41	1925.		Feb. 27	1.07
Sept. 24	1.72	Nov. 17	1.72				
Sept. 26	1.41	Nov. 19	1.72	Jan. 13	1.15	Mar. 13	1.07
Sept. 27	1.07	Nov. 20	1.07	Jan. 15	1.07	Mar. 14	0.96
Sept. 28	1.07	Nov. 21	1.41	Jan. 16	1.00	Mar. 15	0.96
Sept. 29	1.07	Nov. 22	1.41	Jan. 17	0.85	Mar. 16	1.15
Sept. 30	1.07	Nov. 23	1.07	Jan. 18	1.07	Mar. 17	1.31
		Nov. 24	1.07	Jan. 19	0.85	Mar. 18	1.15
Oct. 1	1.41	Nov. 25	1.41	Jan. 20	1.07	Mar. 19	1.15
Oct. 2	1.07	Nov. 26	1.07	Jan. 21	1.07	Mar. 24	1.15
Oct. 14	1.72	Nov. 27	1.07	Jan. 23	1.07	Mar. 26	1.07
Oct. 15	1.72	Nov. 28	0.53	Jan. 26	1.07		
Oct. 17	1.41	Nov. 29	0.53	Jan. 27	0.96	April 11	1.24
Oct. 18	1.41					April 12	1.15
Oct. 21	1.72	Dec. 14	1.07	Feb. 10	1.07	April 13	1.41
Oct. 22	2.27	Dec. 19	1.00	Feb. 11	1.07	April 14	1.24
Oct. 23	1.72	Dec. 20	1.07	Feb. 16	1.41	April 15	1.07
Oct. 26	1.72	Dec. 23	1.07	Feb. 17	1.41	April 16	1.15
Oct. 27	1.72	Dec. 26	1.00	Feb. 18	1.24	April 24	1.07

The observations in general were made at Mr. Babcock's house on the northern outskirts of Pasadena, except in the following cases :—

October 2, 1924, on Mt. Wilson.—This gave a value not very different from that obtained on previous nights in Pasadena.

November 28 and November 29, 1924, at Balboa Island.—Of these Mr. Babcock says :—"These readings at Balboa Island, in Newport Harbour, some 50 miles south of Pasadena, were made under exceptionally good conditions. I took great pains to assure myself of this correctness, because of the marked difference which appeared. On account of the good agreement found in October between Pasadena and Mt. Wilson, it does not seem probable that the difference shown here is due to artificial light at Pasadena."

Subject to any reservation that may be necessary on this last head, it appears that, as was expected, the auroral light is ordinarily much brighter in California than in England. The mean intensity comes out at 1.24, as compared with 0.562 for the same quantity in England. It appears, then, that the auroral intensity in California averages about 2.2 times that in England. It is necessary to remind the reader that by auroral intensity is here meant the intensity transmitted by the auroral filter. This consists of two parts, the aurora line itself and the portion of continuous spectrum, perhaps 150A broad, on which it appears. I have at present no satisfactory means of estimating how much this contamination with continuous spectrum contributes to the total light transmitted.

This striking difference emphasises the need of observations over a wide range of localities. A scheme has been already organised by the writer for this purpose. About twelve instruments have been inter-compared and distributed to friends and correspondents in different parts of the world who have promised to take regular observations.

If we take the highest reading observed by Mr. Babcock, 2.27 (October 22, 1924), and the lowest yet observed by me, 0.255, we get a total variation of about *ninefold* in the auroral intensity.

There is some indication of correlation between Mr. Babcock's auroral intensities and those measured on the same day in England ; but the number of days on which observations were secured in both places is only 37, which is hardly enough for satisfactory discussion. This point is accordingly deferred until more observations are available.

[*Note added September 23, 1925.*—It will be noticed in examining the tables that high values of the various components tend to occur in the late autumn, and low values in the early spring, with a mean value about the end

of November. Thus, to take the auroral component, which has been under observation the longest, low values occur in the spring of 1923-1924-1925, and high ones in the autumn of 1923 and 1924. Since this paper was written I have obtained high values for the autumn of 1925. This has gone far to confirm a suspicion which I did not wish to mention without this additional evidence, namely, that there is a marked annual periodicity in this and the other components of the night sky. Mr. Babcock's observations in California show the same seasonal variation. Fuller discussion is reserved for the present.]

§11. *Summary.*

This paper recapitulates, with small correction, and continues the series of observations of the night sky in England initiated in 'Roy. Soc. Proc.,' A, vol. 106, p. 117, 1924. The series now extends over nearly $2\frac{1}{2}$ years. As before, the intensities of the various chromatic components of the light are found to undergo important variations when measured against a fixed terrestrial standard. These components also undergo considerable relative variations when measured against one another.

The extreme ranges so far encountered are :—

For the orange red component	3·7 to 1.
For the auroral component (region near $\lambda 5578$) ..	4·7 to 1.
Blue component	2·6 to 1.

Attention is primarily concentrated on the spectral region transmitted by a screen designed to isolate the green auroral line as nearly as possible. Notwithstanding the definite relative variations, this auroral intensity is rather highly correlated with the intensity in the orange-red region, not quite so highly with the blue region, and still less, though quite definitely, with the photographic region centred near $\lambda 4300$.

The values found for the correlation coefficients are :—

Aurora-red, 0·70. Aurora-blue, 0·66. Aurora-photographic, 0·44.

On the other hand, the auroral intensity is not correlated appreciably with the degree of magnetic disturbance or the height of the barometer. The connection with the sun-spots, if any, is not yet apparent.

The intensity does not vary measurably with the sun's distance below the horizon, within the limits, evening and morning, when twilight is excluded.

Parallel observations of the auroral intensity over some months have been

made by Mr. H. D. Babcock, at Pasadena, and at Mt. Wilson, California. The values there are in the mean more than double those prevailing in England.

An extended scheme for observations over the globe has been organised, with the promised help of friends and correspondents, to whom the instruments have already been handed over.

There is considerable suspicion of an annual periodicity, high values occurring before the end of November, and low values afterwards.

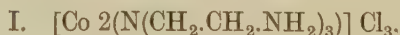
β β' β'' -Triaminotriethylamine and its Complex Metallic Compounds.

By F. G. MANN, Ph.D., and Sir W. J. POPE, F.R.S.

(Received August 17, 1925.)

We have recently shown ('Roy. Soc. Proc.,' A, 1924, vol. 107, p. 80) that 1 : 2 : 3-triaminopropane forms co-ordination compounds with certain trivalent metals, such as cobalt and rhodium ; these compounds are of the general type of *bis*-propanetriamine cobaltic chloride, $[\text{Co } 2(\text{NH}_2\text{.CH}(\text{CH}_2\text{.NH}_2)_2)] \text{Cl}_3$, in accordance with Werner's theory of co-ordination. In these compounds the triaminopropane behaves in a similar way to ethylenediamine, each amino-group taking part in the formation of the co-ordinated radicle. It is thus seen that the grouping, $\text{NH}_2\text{.CH}_2\text{.CH.NH}_2$, which is present twice in the triaminopropane molecule, behaves for co-ordination purposes in the same way as the molecule of ethylenediamine, $\text{NH}_2\text{.CH}_2\text{.CH}_2\text{.NH}_2$.

This analogy in behaviour appears worthy of further investigation, and we have therefore studied the manner in which β β' β'' -triaminotriethylamine, $\text{N}(\text{CH}_2\text{.CH}_2\text{.NH}_2)_3$, co-ordinates with the metals ; in this substance the grouping, $\text{NH}_2\text{.CH}_2\text{.CH}_2\text{.N:}$, occurs three times, but it would seem that the presence of the three primary amino-groups has greatly diminished the basic properties of the tertiary amino-radicle, since Ristenpart ('Ber.,' 1896, vol. 29, p. 2530) obtained only salts in which the substance acts as a tribasic amine. It might thus be anticipated that co-ordinated salts of the type I would be formed.



This, however, is not the case, and the triaminotriethylamine acts in all cases for co-ordination purposes as a tetrabasic amine ; we have thus been

able to prepare such salts as dichloro-triaminotriethylamine-platinic dichloride, II, and triaminotriethylamine-platinous di-iodide, III.



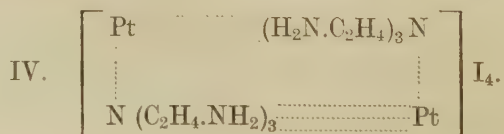
This result is remarkable in that simple tertiary aliphatic amines such as triethylamine do not yield co-ordination compounds, whilst the tertiary nitrogen atom in triaminotriethylamine does act as a co-ordinating unit. It is suggested that a steric reason exists for this fact, namely, that the attachment of the three amino-groups, NH_2 , at three apices of the octahedral co-ordinated group in Formula II, say, at positions 1 : 2 : 4, may bring the tertiary nitrogen atom into position 3 and thus facilitate its co-ordination. Such an explanation does not serve in the case of the platinous compound III, in which, according to Werner, the four co-ordinating radicles should lie in a plane with the platinum atom ; further discussion of the configuration of this compound may be postponed until we are able to determine the molecular weight of some substance of the same type.

The preparation of triaminotriethylamine described by Ristenpart is a tedious one and a more expeditious method was therefore sought in the direct reduction of $\alpha\alpha'\alpha''$ -tricyanotrimethylamine, which Dubsky prepared ('Ber.,' 1916, vol. 49, p. 1041) by treating a cold aqueous solution of hexamethylenetetramine and potassium cyanide with strong hydrochloric acid, when the trinitrile separates on standing in high yield. Many attempts were made to repeat Dubsky's preparation, but on only one occasion was the trinitrile obtained, and then in minute yield. The preparation was therefore carried out by Curtius's modification ('Jour. prak. Chem.,' 1917, vol. 96, p. 232) of Eschweiler's method ('Ann.,' 1894, vol. 278, p. 233), in which free hydrogen cyanide is used instead of potassium cyanide. This preparation proceeds smoothly, and gives the tricyanotrimethylamine in good yield. Numerous attempts were made to reduce this compound to triaminotriethylamine, but all failed. Sodium and absolute ethyl or amyl alcohol decomposed the compound rapidly with the production of ammonia, whilst aluminium amalgam had no apparent action on a boiling aqueous alcoholic solution. This attempted preparation of the base was therefore abandoned, and recourse was had to Ristenpart's method. Considerable improvements have been made in this method, particularly in the hydrolysis of the triphthalimidotriethylamine, and the base has thus been prepared in large amount. It was found, however, that triaminotriethylamine may act either as a triamine or as a

tetramine : a strong solution in dilute hydrochloric acid if poured into alcohol precipitates the trihydrochloride, $N(C_2H_4NH_2)_3 \cdot 3HCl$, as Ristenpart describes, but if concentrated and allowed to crystallise yields the tetrahydrochloride, $N(C_2H_4NH_2)_3 \cdot 4HCl, H_2O$. Two aurichlorides, two platinichlorides and two rhodochlorides have thus been prepared, in which the amine acts as a tri- and tetra-acidic base respectively. The rhodochlorides are of interest, inasmuch as in both the rhodium acts as a divalent metal. Moreover, triaminotriethylamine acts exclusively as a tetracidic base when it co-ordinates with metals ; and the two series of co-ordination compounds which have been prepared as derivatives of platinic and platinous chlorides, viz., dichlorotriaminotriethylamine-platinic dichloride (II), and triaminotriethylamine platinous di-iodide (III), thus fall strictly into line with the requirements of Werner's theory. In both types the tertiary nitrogen atom has co-ordinated with the metal, and therefore the question of its basicity when the primary amino-groups alone co-ordinate does not arise. No evidence of the formation of compounds of the type (I) has been obtained.

The compounds thus obtained with divalent and tetravalent platinum represent co-ordination compounds of two entirely novel types. They are the first co-ordinated compounds to be prepared with an aliphatic tetramine, and each presents several points of interest. It will be noticed that in the compound dichlorotriaminotriethylamine, platinic dichloride, each β -aminoethyl group in conjunction with the tertiary nitrogen atom acts as a bridging group spanning the distance between two adjacent apices of the platinum octahedron ; the amine thus consists of three bridging groups, all of which have one end in common, viz., the tertiary nitrogen atom. The complex thus formed would appear to have a plane of symmetry, and should therefore not be resolvable into optically active isomerides.

The compound of divalent platinum, triaminotriethylamine-platinous di-iodide (III), is of particular interest because it is difficult to see how the four nitrogen atoms in one molecule of the amine can be arranged at the four corners of a square of which the centre is occupied by the platinum atom, in accordance with the Werner conception. It might be suggested that two molecules of the amine share two atoms of platinum between them and that the constitution of the di-iodide is represented by formula (IV) rather than by (III).



The molecular weight determinations necessary to settle this question are not conveniently made with the sparingly soluble di-iodide. We are at present engaged in the study of a new set of salts of similar constitution and hope thence to derive positive information concerning the molecular weights.

EXPERIMENTAL.

Preparation of Triaminotriethylamine Hydrochloride.

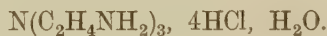
Triphthalimidotriethylamine.

Ristenpart passed dry ammonia gas through molten β -bromethylphthalimide (prepared by Gabriel's method, 'Ber.,' 1889, vol. 23, p. 1137) at 140-150° for 5-8 hours, and extracted the viscous reaction product with boiling alcohol before it cooled and solidified. The alcohol dissolves unchanged bromethylphthalimide and the triphthalimidotriethylamine hydrobromide (approximately 12 per cent.) formed as a by-product, whilst the insoluble residue of triphthalimidotriethylamine is purified by washing with alcohol and water, and recrystallisation from acetic acid. This method is advantageously modified by filling a wide boiling-tube about two-thirds full of the molten bromethylphthalimide and passing in ammonia through a wide delivery tube. After about eight hours the product becomes too viscous to allow the free passage of ammonia, and, after cooling, the tube and contents are pulverised and extracted with boiling alcohol. The extraction is repeated to ensure the removal of unchanged bromethylphthalimide from the insoluble residue, and the latter is then recrystallised from acetic acid. Triphthalimidotriethylamine is thus obtained of m.p. 193° (corr.) (Ristenpart gives m.p. 187·5°); addition of dry ether to the acetic acid mother liquors throws out a further crop of the triphthalimido compound, usually of a cream colour, and this material without further purification also gives the pure hydrochloride of the base on hydrolysis.

Triaminotriethylamine hydrochloride.—Ristenpart directs that the triphthalimidotriethylamine should be hydrolysed by heating 2 grm. portions with 5 c.c. of concentrated hydrochloric acid in a sealed tube for two hours at 150°. The compound is more expeditiously hydrolysed by boiling in 15 gram lots with 300 c.c. of dilute hydrochloric acid (1 : 1 by volume) very gently for about seven hours. On cooling the clear solution, phthalic acid separates, and the filtrate, after concentration to small bulk, is poured into alcohol, when the trihydrochloride separates as a fine white powder. (Found : Cl = 41·44. $C_6H_{21}N_4Cl_3$ requires Cl = 41·60 per cent.) If, however, the concentrated aqueous solution is allowed to cool, large spear-shaped crystals of the hydrated

triaminotriethylamine tetrahydrochloride, $N(C_2H_4NH_2)_3$, 4HCl, H_2O , separate. The crystals of the tetrahydrochloride melt at $167\text{--}169^\circ$ with effervescence, giving off steam and hydrogen chloride, whilst the residue resolidifies to a white mass of the trihydrochloride. The tetrahydrochloride effloresces on exposure to the air for several days, giving the trihydrochloride; the same change occurs rapidly when the crystalline material is heated *in vacuo* at 100° . (Found: C = 23.40; H = 7.84; Cl = 45.40; N = 17.78; loss on heating *in vacuo* at 80° = 17.28. $C_6H_{24}O \cdot N_4Cl_4$ requires C = 23.22; H = 7.81; Cl = 45.75; N = 18.07, HCl + H_2O = 17.58 per cent.)

The following report has been prepared by Mr. J. Reekie, B.A., working under the direction of Mr. A. Hutchinson, F.R.S. :—

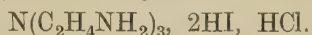


“The substance crystallises in hexagonal prisms terminated at each end by acute hexagonal pyramids. No indications of hemimorphism or hemihedrism were observed, and no other forms were exhibited. The crystals may, therefore, be assigned to the holohedral class of the hexagonal system.

“Forms $m\{10\bar{1}0\}$ and $p\{10\bar{1}1\}$. Angle $mp = 10\bar{1}0 : 10\bar{1}1 = 15.39\frac{1}{2}$ whence $a : c = 1 : 3.093$.

“There is a moderate cleavage parallel to the basal plane. A uniaxial interference figure of negative sign was observed through a cleavage plate. The indices of refraction were measured by means of a prism formed by two opposite p faces. For sodium light they are $o = 1.5949$, $e = 1.5813$. Sp. gr. $\frac{15^\circ}{4^\circ} = 1.389$.”

In the preparation of the above base, large quantities of triphthalimidotriethylamine hydrobromide accumulated. Efforts were made to hydrolyse this compound similarly by boiling under reflux with hydrochloric and with hydrobromic acid. The hydrobromide proved surprisingly resistant to such treatment, and for successful hydrolysis recourse was had to Ristenpart's method, whereby the hydrobromide is heated in a sealed tube with a mixture of acetic and strong hydrobromic acids, and the pure triaminotriethylamine trihydrobromide was thus obtained. We were unable to obtain a tetrahydrobromide by recrystallising the trihydrobromide from strong hydrobromic acid.

Triaminotriethylamine Dihydriodide Monohydrochloride.

On mixing strong aqueous solutions of the tri- or tetra-hydrochloride and of potassium iodide, a fine white crystalline deposit separates. The latter on recrystallisation from a little hot water furnishes dense white crystals of *triaminotriethylamine dihydriodide monohydrochloride*, which do not melt below 300° . (Found : C = 16.43 ; H = 4.67, Cl + 2I = 65.63, N = 12.35. $\text{C}_6\text{H}_{21}\text{N}_4\text{ClI}_2$ requires C = 16.42, H = 4.83, Cl + 2I = 65.93, N = 12.77 per cent.) It was thought that the formation of this mixed salt even by a large excess of potassium iodide might have been caused by the precipitation of the mixed salts before the trihydriodide had time to be formed. To prevent this a concentrated aqueous solution of the tetrahydrochloride was heated to boiling and a boiling solution of potassium iodide saturated in the cold added. The clear solution, after heating to 100° , was allowed to cool, when the same mixed salt separated and after recrystallisation was free from potassium iodide. (Found : C = 15.96 ; H = 4.58 per cent.)

Tricarbamidotriethylamine. $\text{N}(\text{C}_2\text{H}_4\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_3$.

A slight excess of silver cyanate was added to an aqueous solution of triaminotriethylamine trihydrochloride, and the mixture heated on the water-bath for 20 minutes. The solution was then filtered and evaporated to small bulk ; on cooling a crystalline deposit coloured violet by a trace of silver was obtained. After drying and extracting the deposit with boiling absolute alcohol, filtering and cooling, a voluminous white crystalline mass separated. The latter on heating shrinks at 140° and finally melts with decomposition at 167 – 168° . (Found : C = 39.44 ; H = 7.70. $\text{C}_3\text{H}_{21}\text{O}_3\text{N}_7$ requires C = 39.20 ; H = 7.68 per cent.) *Tricarbamidotriethylamine* is very soluble in cold water and in warm acetic acid, but only moderately soluble in boiling alcohol ; it is almost insoluble in boiling benzene, ether and acetone. On exposure to light for several days it becomes brown.

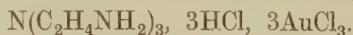
The pharmacological properties of the base have been investigated by Mr. J. H. Wadia, B.A., B.Sc., who reports that “Triaminotriethylamine trihydrochloride has the typical action of ammonium salts. This is shown in particular by the stimulation of the medulla in animals, the respiration becoming quicker and deeper. Like ammonium chloride, this amine exerts no toxic action and produces no symptoms when given to rabbits intravenously in doses of 5 c.c. of a 2 per cent. solution for an animal of about 2 kgm. in weight.”

A pure aqueous solution of the free base cannot be prepared by steam-distilling a solution of the hydrochloride neutralised with caustic soda, for the base is not volatile in steam.

It was considered possible that triaminotriethylamine trihydrochloride, when heated above its melting-point, would lose ammonium chloride and form either N-aminoethylpiperazine or even triethylenediamine, a reaction parallel to Ladenburg's synthesis of piperidine by the pyrogenic decomposition of tetramethylene-diamine dihydrochloride ('Ber.,' 1885, vol. 18, p. 3100; 'Ann.,' 1888, vol. 247, p. 54). Some preliminary experiments showed, however, that when the trihydrochloride was heated to about 400° C. in a metal bath, it slowly decomposed to a black mass. If, however, the trihydrochloride in portions of not more than 0.2 gm. is placed in a test tube, and the bottom of the latter rotated quickly above a small Bunsen flame for a few seconds, the hydrochloride melts to a brown liquid which effervesces, whilst a brownish-white sublimate forms on the cooler portions of the tube. If the heating is very brief, the brown liquid suffers little charring, and on cooling solidifies to a brown mass. A number of tubes of the hydrochloride were thus treated, and when cool the ends were cut off below the condensed sublimate. The ends were extracted with boiling water containing a little animal charcoal, and on filtering a clear pale yellow solution was obtained. This solution readily gave a crystalline platinichloride and picrate, but the product in each case proved on investigation to be a mixture of at least two compounds. Owing to the small amount of material available, no further attempts to separate and identify the constituents were made.

Compounds of triaminotriethylamine with the chlorides of various heavy metals were prepared and those obtained with the noble metals were used to study the further co-ordination of the base with the metal itself, the compounds of platinum finally being chosen as most suitable for this purpose. It will be seen that the chlorides of the noble metals usually form two derivatives with triaminotriethylamine, *i.e.*, with the tri- and tetra-hydrochloride of the base respectively.

Aurichloride of Triaminotriethylamine trihydrochloride.



When an aqueous solution of the trihydrochloride is added to that of an excess of potassium aurichloride, the triaurichloride of the above composition is precipitated as Ristenpart describes. (Found: Au = 50.88. $\text{C}_6\text{H}_{21}\text{N}_4\text{Cl}_{12}\text{Au}_3$ requires Au = 50.75 per cent.). This compound separates in orange-

coloured needles, which are freely soluble in water, and exceedingly so in alcohol and acetone. If an attempt is made to recrystallise the triaurichloride from hot water, the solution rapidly changes to a pale yellow colour and deposits on cooling a finely crystalline lemon-yellow solid. The gold content of this material becomes higher the longer the aqueous solution is boiled; after heating for about thirty minutes, complete decomposition ensues, and metallic gold is deposited, the solution becoming almost colourless. Several further instances will be given in which the amine thus acts as a vigorous reducing agent towards the chlorides of the heavy metals. The triaurichloride is stable whilst protected from damp; when, however, it is placed *in vacuo* over sulphuric acid, the colour rapidly darkens and eventually becomes a uniform russet-brown. This is apparently only a physical change. A specimen of the triaurichloride was kept *in vacuo* for a week, by which time the change in colour was complete; the melting-point of the russet-brown material had fallen only one degree, whilst the gold content remained unchanged. (Found: Au = 50.95 per cent.)

Aurichloride of the tetrahydrochloride $N(C_2H_4NH_2)_3, 4HCl, 2AuCl_3$.

An attempt was made to prepare the tetraurichloride by dissolving 0.6 gram. of the trihydrochloride in 20 c.c. of dilute hydrochloric acid (1 : 1 by volume), and adding this solution rapidly to that of 5 grms. of chlorauric acid ($HAuCl_4, 3H_2O$) in 20 c.c. of hydrochloric acid of the same strength. The mixture rapidly gave a pale yellow deposit. After standing one hour, the solution was filtered, and the residue washed with hydrochloric acid of the above strength until the washings contained no free chlorauric acid. The residue was dried *in vacuo* over sulphuric acid and caustic soda, and was thus obtained as a pale yellow crystalline solid which melted with decomposition at 187–189°. This compound on analysis gives low but consistent values for carbon; the identity of the compound is placed beyond doubt by the values obtained for all other elements. (Found: C* = 7.29, 7.17; H = 2.56, 2.58; Au = 44.06, 43.68; Cl = 39.07; N = 6.20. $C_6H_{22}N_4Cl_{10}Au_2$ requires C = 8.00; H = 2.45; Au = 43.85; Cl = 39.43; N = 6.23 per cent.). It is not unusual for the aliphatic polyamines to form aurichlorides of lower gold content than their basicity demands. 1 : 2 : 3 Triamino-propane unites with only one equivalent of aurichloric acid (Mann and Pope, *loc. cit.*, p. 83).

* Whenever in this paper more than one value is given for an element, the values refer to analyses of different preparations of the compound, and not merely to repeated analyses of the same sample.

Triaminotriethylamine Mercurichloride $N(C_2H_4NH_2)_3, 3HCl, 5HgCl_2$.

A solution of 1.0 gm. of the trihydrochloride in 10 c.c. of water was added to 90 c.c. of a saturated aqueous solution of mercuric chloride. Fine colourless needles slowly separated, and after thirty minutes were filtered, washed with water and air-dried. The *penta-mercurichloride* melts with decomposition at 202-204°. (Found: N = 3.58; Cl = 28.29. $C_6H_{21}N_4Cl_{13}Hg_5$ requires N = 3.47; Cl = 28.57 per cent.).

Rhodiochloride of Triaminotriethylamine Trihydrochloride.

A solution of 1.5 grms. of triaminotriethylamine trihydrochloride was added to an equimolecular quantity (3.21 grms.) of sodium rhodiochloride ($Na_3RhCl_6, 9H_2O$) dissolved in 100 c.c. of water. A pink and apparently amorphous precipitate separated at once, and after standing for five minutes was filtered and well washed with water, alcohol and ether. It was then dried *in vacuo* and obtained as a fine salmon-pink powder. Although this preparation was repeated several times, on only one occasion was the product obtained crystalline, when the precipitated material, on standing unfiltered for five hours, was slowly converted into beautiful garnet-red crystalline scales. The *rhodiochloride* thus obtained has an abnormal composition, since the rhodium acts as a divalent metal. (Found: C = 12.71, 12.72, 12.36; H = 4.72, 4.84, 4.76; Cl = 37.30, 37.24; $H_2O = 9.74, 9.78$. $C_{12}H_{54}O_6N_8Cl_{12}Rh_3$ requires C = 12.63; H = 4.77; Cl = 37.30; $H_2O = 9.48$ per cent.) The anhydrous material shrinks in bulk at 257°, swells up into a pale yellow mass at 260°, and finally melts to a pale brown liquid at 280°.

When the trihydrochloride of the base is added to one-half or to twice the above proportion of sodium rhodiochloride, the same salmon-pink product is produced. (Found: using one-half the equimolecular quantity of the rhodiochloride, C = 12.43; H = 4.73: using twice the equimolecular quantity, Cl = 37.01 per cent.)

Rhodiochloride of the Tetrahydrochloride. $N(C_2H_4NH_2)_3, 4HCl, 2RhCl_2$.

Several attempts were made to prepare a co-ordinated derivative of rhodium with triaminotriethylamine by boiling the previous rhodiochloride with a solution of the free base or its trihydrochloride. Such experiments led always to the decomposition of the rhodiochloride, and were eventually abandoned; they resulted, however, in the preparation of a rhodiochloride of the base, in which

the latter acts as a tetramine and the rhodium again as a divalent metal. Thus 5.0 grms. of the former rhodichloride, $2\text{N}(\text{C}_2\text{H}_4\text{NH}_2)_3$, 3HCl , 3RhCl_2 , $6\text{H}_2\text{O}$, were boiled with 35 c.c. of water for five hours under reflux. The rhodichloride rapidly decomposed, and a fine black precipitate containing rhodium separated. The solution was filtered, and on cooling deposited a second small crop of the black powder. The solution, now of a very pale pink colour, was again filtered, and evaporated to small bulk. On cooling, there separated a yellowish-grey deposit, which when once precipitated became quite insoluble in water. This material was filtered, washed repeatedly with boiling water, then with alcohol and ether, and then dried. If the original aqueous solution is concentrated too far before cooling, this product separates mixed with a viscous gum, which renders further treatment very difficult. The *rhodichloride* is thus obtained as a pale yellowish-grey amorphous powder which remains unchanged on heating to 300° . (Found: C = 11.21, 11.20; H = 3.48, 3.40. $\text{C}_6\text{H}_{22}\text{N}_4\text{Cl}_3\text{Rh}_2$ requires C = 11.26; H = 3.47 per cent.)

Rutheniochloride of the Tetrahydrochloride. $\text{N}(\text{C}_2\text{H}_4\text{NH}_2)_3$, 4HCl , 2RuCl_3 , $2\text{H}_2\text{O}$.

An aqueous solution of the trihydrochloride was added to a considerable excess of a dilute solution of ruthenium chloride in hydrochloric acid, when a fine reddish-brown amorphous precipitate rapidly separated. The solution was then placed in a warm water-bath for about one minute, and well stirred. The precipitate redissolved and fine crystalline scales separated from the solution. The latter was immediately withdrawn from the water-bath and rapidly filtered, when it continued to deposit the crystalline scales until cold. Very great care is required to attain the conditions necessary for the conversion of the amorphous to the crystalline product. If the ruthenium solution is too concentrated, or if the mixture is not heated sufficiently, the amorphous precipitate forms a slimy reddish-black product; if the mixture is heated too long or to too high a temperature, the precipitate decomposes to a fine black granular mass, and the solution becomes deep brownish-black in colour. The crystalline precipitate, when filtered, washed with water, and dried *in vacuo*, is obtained in minute bronze-coloured crystals, which when heated slowly darken in colour to a black mass, which does not melt below 280° . (Found: C = 9.76; H = 3.55; Cl = 47.33. $\text{C}_6\text{H}_{26}\text{O}_2\text{N}_4\text{Cl}_{10}\text{Ru}_2$ requires C = 9.67; H = 3.52; Cl = 47.64 per cent.) In this compound the amine acts as a tetracidic base: the composition of the rutheniochloride is therefore strictly parallel to that of the rutheniochlorides of the mono- and di-acidic bases prepared by Gutbier ('Zeit. anorg. Chem.,' 1923, vol. 129, p. 86), who found that quinoline

and ethylenediamine, for example, give rutheniochlorides of composition $4\text{C}_3\text{H}_7\text{N}$, 4HCl , 2RuCl_3 , and $2\text{C}_2\text{H}_4(\text{NH}_2)_2$, 4HCl , 2RuCl_3 respectively.

Platinochloride of Triaminotriethylamine Trihydrochloride.



This compound was prepared for use in the further preparation of co-ordinated derivatives of the base and divalent platinum, but its use was subsequently abandoned in favour of that of potassium platinochloride. An aqueous solution of the trihydrochloride was shaken for several hours with an excess of freshly precipitated silver platinochloride; the mixture was then filtered, and the clear red solution diluted with alcohol. A pink emulsion was thus produced which passed freely through filterpaper, but when chilled in ice-water for two hours slowly deposited pink crystalline flakes. These were filtered, and recrystallised from a little hot water, from which the *platinochloride* separated in deep red crystalline leaflets. (Found: C = 10.60; H = 3.55; Pt = 42.85; $\text{C}_{12}\text{H}_{48}\text{O}_3\text{N}_8\text{Cl}_{12}\text{Pt}_3$ requires C = 10.60, H = 3.56, Pt = 43.13 per cent.)

Platinichloride of Triaminotriethylamine Trihydrochloride.



Ristenpart describes an anhydrous platinichloride of the above type as crystallising in six-sided plates, which shrink at 250° and melt with decomposition at 280° . The compound of the above composition was prepared by slowly adding a solution of the trihydrochloride to a solution of pure sodium platinichloride ($\text{Na}_2\text{PtCl}_6, 6\text{H}_2\text{O}$), when a crystalline precipitate rapidly separated. The latter was filtered, washed with water and alcohol and dried in air. The platinichloride of the trihydrochloride is thus obtained in orange-coloured needles. It is paler in colour than that of the tetrahydrochloride, and is only slightly soluble in cold water. (Found: C = 8.55; H = 3.63; Pt = 34.41; $\text{H}_2\text{O} = 10.73$. $\text{C}_{12}\text{H}_{62}\text{O}_{10}\text{N}_8\text{Cl}_{18}\text{Pt}_3$ requires C = 8.46; H = 3.67; Pt = 34.41; $\text{H}_2\text{O} = 10.58$ per cent.) The anhydrous material darkens in colour at 225° and melts, with decomposition and foaming, at $231\text{--}232^\circ$; it therefore differs markedly from Ristenpart's anhydrous product. If in the preparation either of the two solutions contains any free hydrochloric acid, the platinichloride is always contaminated with that of the tetrahydrochloride described below.

Platinichloride of the Tetrahydrochloride. $\text{N}(\text{C}_2\text{H}_4\text{NH}_2)_3, 4\text{HCl}, 2\text{PtCl}_4, 10\text{H}_2\text{O}.$

If a solution of the trihydrochloride is added to a solution of an excess of pure chloroplatinic acid ($\text{HPtCl}_6.6\text{H}_2\text{O}$), or if a solution of the tetrahydro-

chloride is added to that of chloroplatinic acid containing much hydrochloric acid, the platinichloride of the tetrahydrochloride is in both cases precipitated as a fine powder, which when recrystallised from hot water separates in deep orange-coloured crystals. The latter lose their water of crystallisation when heated *in vacuo* at 80° ; when heated above 80° the compound undergoes partial decomposition with darkening in colour and considerable loss in weight. (Found: For product from trihydrochloride and pure chloroplatinic acid: C = 6.79, 6.87; H = 3.11, 3.04; Cl = 39.98; Pt = 36.87, 36.70; H_2O = 8.62. For product precipitated in excess of hydrochloric acid: C = 6.88, H = 3.07, Cl = 40.28, Pt = 37.19, 36.70. $C_6H_{32}O_5N_4Cl_{12}Pt_2$ requires C = 6.82; H = 3.05; Cl = 40.28; Pt = 36.96; H_2O = 8.53 per cent.) The anhydrous material is very hygroscopic, darkens in colour at 260° and melts with decomposition to a voluminous black mass at $271-273^{\circ}$.

The Metallic Co-ordinated Derivatives of Triaminotriethylamine.

In the formulæ given below the contraction "tren" is used to denote one molecule of triaminotriethylamine, *i.e.* $N(C_2H_4NH_2)_3$.

Co-ordinated Derivatives of Tetravalent Platinum.

Dichlorotriaminotriethylamine-platinic-dichloride, $[Cl_2Pt\ tren] Cl_2$.

This compound is best prepared by the action of an excess of triaminotriethylamine trihydrochloride on the platinichloride of the tetrahydrochloride described above. The platinichloride (12 grms.) and the trihydrochloride of the base (12 grms., *i.e.*, four molecular proportions) are dissolved in 240 c.c. of hot water, and the clear solution boiled under reflux for 14 hours, by the end of which time a fine deposit of the co-ordinated compound has separated. Water (90 c.c.) is now added, and on heating the solution again becomes clear; after boiling for a further two hours, the solution is filtered hot, and on cooling deposits *dichlorotriaminotriethylamine-platinic-dichloride* as a yellowish-orange powder. This is recrystallised from hot water (80 c.c.), and from the filtered solution the dichloride separates as dense orange-coloured crystals (2.9 grms.) (Found: C = 14.73; H = 3.76; Pt = 40.36, 40.24, 40.26, ionised Cl = 14.39, total Cl = 29.45. $C_6H_{18}N_4Cl_4Pt$ requires C = 14.90, H = 3.75; Pt = 40.39; ionised Cl = 14.67, total Cl = 29.35 per cent.)

If the triaminotriethylamine trihydrochloride and the platinichloride are heated together in hydrochloric acid (1 : 1 by volume) no reaction occurs, and even after 20 hours' boiling the platinichloride crystallises out unchanged on cooling. If, on the other hand, the solution of the trihydrochloride is neutralised

with the calculated quantity of normal caustic soda solution, decomposition occurs on warming with production of a brownish black solution.

The dichloride when rapidly crystallised from warm water separates in small heavy pale orange crystals, which darken in colour at about 240° and melt with foaming at $263\text{--}266^{\circ}$. If the concentration of the solution is such that the crystallisation occurs slowly over a period of about 24 hours, the dichloride separates in well-defined bunches of pale yellow characteristically heart-shaped twins. The mother liquor from such a preparation when allowed to stand in a closed vessel for several weeks deposits heavy many-sided (almost spherical) dark orange crystals, which are probably formed by repeated twinning of the pale yellow form; both melt with decomposition at $263\text{--}266^{\circ}$. The dichloride is freely soluble in hot water, slightly so in cold water, and insoluble in boiling alcohol and acetone; it can also be prepared, although in smaller yield and of less purity, by adding an excess of the trihydrochloride directly to a solution of chloroplatinic acid, and boiling the mixture for several hours.

Dichlorotriaminotriethylamine-platinic di-iodide, $[\text{Cl}_2\text{Pt tren}] \text{I}_2$.

A warm aqueous solution of the dichloride is slowly added to potassium iodide solution saturated in the cold and heated to 80° , when the mixture becomes reddish-brown and deposits deep red crystals. These when filtered off and recrystallised from hot water, yield the *dichlorotriaminotriethylamine platinic di-iodide* in minute dark red crystals, which when dry darken in colour at 225° and decompose to a black mass at $233\text{--}237^{\circ}$. (Found: $\text{Pt} = 29.14$, $\text{C}_6\text{H}_{18}\text{N}_4\text{Cl}_2\text{I}_2\text{Pt}$ requires $\text{Pt} = 29.29$ per cent.)

Dichlorotriaminotriethylamineplatinic platinichloride, $[\text{Cl}_2\text{Pt tren}] \text{PtCl}_6, 2\text{H}_2\text{O}$.

Crystalline flakes of the platinichloride are rapidly deposited when a warm aqueous solution of the dichloride is added to excess of warm chloroplatinic acid solution. On filtering, washing with water and drying in the air, the *platinichloride* is obtained in orange-brown crystalline flakes, which darken in colour at 275° and melt to a black mass with foaming at $287\text{--}288^{\circ}$. (Found: $\text{C} = 8.39$; $\text{H} = 2.71$; $\text{Pt} = 45.37$. $\text{C}_6\text{H}_{22}\text{O}_2\text{N}_4\text{Cl}_8\text{Pt}_2$ requires $\text{C} = 8.41$; $\text{H} = 2.59$; $\text{Pt} = 45.58$ per cent.)

Dichlorotriaminotriethylamineplatinic platinocyanide, $[\text{Cl}_2\text{Pt tren}] \text{Pt}(\text{CN})_4$.

When warm solutions of the dichloride (1 grm. in 30 c.c.) and potassium platinocyanide (2 grms. in 15 c.c.) are mixed a faint opalescence develops, and

after two to three hours long colourless needles of the pure *platinocyanide* are deposited. These dissolve with difficulty in hot water, but partial solution occurs on boiling for several minutes with water. This solution on filtering deposits the *platinocyanide* in two distinct types of crystal, viz., in long white needles and in minute canary-yellow crystals. Analysis indicates that these two forms have the same composition, so that the difference is probably due to dissimilar crystalline habit, in which respect the *platinocyanide* closely resembles the dichloride itself. The colourless needles of the *platinocyanide* darken at 225° , but the pale grey residue does not melt below 300° . (Found : C = 16.85 ; H = 2.64 ; Pt = 54.66. $\text{C}_{10}\text{H}_{18}\text{N}_8\text{Cl}_2\text{Pt}$ requires C = 16.87 ; H = 2.55 ; Pt = 54.87 per cent.)

Co-ordinated Derivatives of Divalent Platinum.

Triaminotriethylamineplatinous platinochloride, $[\text{Pt tren}] \text{PtCl}_4$.

Triaminotriethylamine trihydrochloride (0.9 gm.) is dissolved in water (10 c.c.) and the acid neutralised by adding normal caustic soda solution (11.15 c.c.). This solution is added to two molecular proportions (3 grms.) of potassium platinochloride dissolved in warm water (20 c.c.) and the mixture shaken for seven hours. A pale rose-grey amorphous precipitate slowly separates, and is filtered from the ruby-red mother liquor, washed with water, alcohol and ether and dried *in vacuo*. *Triaminotriethylamineplatinous platinochloride* is thus obtained as a very pale pink amorphous powder, which shrinks at 265° with gradual darkening in colour, giving a charred residue melting at $270\text{--}275^{\circ}$; it is insoluble in cold or hot water. (Found : C = 10.45 ; H = 2.90 ; Pt = 57.44. $\text{C}_6\text{H}_{18}\text{N}_4\text{Cl}_4\text{Pt}_2$ requires C = 10.61 ; H = 2.67 ; Pt = 57.54 per cent.)

Triaminotriethylamineplatinous di-iodide, $[\text{Pt tren}] \text{I}_2$.

The above insoluble platinochloride is formed from the free base with excess of potassium platinochloride. If, however, the amine itself is in excess, the platinochloride, which is first precipitated, reacts further with the base, all the platinum becoming co-ordinated with the amine. Potassium platinochloride (4 grms.) dissolved in warm water (20 c.c.) is added to two molecular proportions (5 grms.) of triaminotriethylamine trihydrochloride in the equivalent volume (58.7 c.c.) of normal caustic soda solution. On heating on the water-bath, the triaminotriethylamineplatinous platinochloride separates and slowly redissolves until after about three hours a clear, colourless solution results.

Only minute quantities of solid product are obtained by partly evaporating this solution, but after concentrating to one-third of the original volume and adding it at boiling temperature to an equal volume of hot potassium iodide solution (saturated in the cold), a heavy white powder separates on cooling. This is filtered, washed with water, in which it is appreciably soluble when freshly prepared, then with alcohol and ether and dried *in vacuo*. The hydrated di-iodide $[\text{Pt tren}] \text{I}_2 \cdot 2\text{H}_2\text{O}$, is thus obtained as a fine white powder; when precipitated in the cold by adding potassium iodide solution to that of the platinum compound, separated as described above, and preserved *in vacuo* over phosphoric anhydride, it yields the pale cream-coloured anhydrous di-iodide. In each case the yield is low. (Found: For the hydrated di-iodide, $\text{I} = 40.23, 40.01$. $\text{C}_6\text{H}_{22}\text{O}_2\text{N}_4\text{I}_2\text{Pt}$ requires $\text{I} = 40.23$. For the anhydrous di-iodide, $\text{C} = 11.91$; $\text{H} = 3.14$; $\text{Pt} = 32.64$. $\text{C}_6\text{H}_{18}\text{N}_4\text{I}_2\text{Pt}$ requires $\text{C} = 12.10$; $\text{H} = 3.05$; $\text{Pt} = 32.79$ per cent.) The anhydrous salt darkens at 260° and melts with decomposition at $267\text{--}269^\circ$; the hydrated compound swells at about 120° and has then the same melting-point as the anhydrous di-iodide. Although the iodide when freshly precipitated will redissolve in the mother liquor on warming, it is only slightly soluble in boiling water after drying, and from the solution so obtained the di-iodide usually separates as a sticky film which only slowly solidifies.

Action of Triaminotriethylamine Trihydrochloride on Magnus's Green Salt.

It was considered possible that an excess of amine, on prolonged boiling with tetrammino-platinous platinochloride $[\text{Pt}(\text{NH}_3)_4] \text{PtCl}_4$, would displace the ammonia and co-ordinate with both the atoms of platinum. Magnus's salt (4 grms.) was therefore added to four molecular proportions (3.4 grms.) of the trihydrochloride dissolved in water (60 c.c.), and the whole boiled under reflux for eight hours, when some of the Magnus's salt remained unchanged, whilst much metallic platinum had been precipitated. After filtration the pale yellow solution deposited on cooling fine yellow needles of the trans-compound, platosammine chloride $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. (Found: $\text{Pt} = 64.60$. $\text{H}_6\text{N}_2\text{Cl}_2\text{Pt}$ requires $\text{Pt} = 65.01$ per cent.) The dichlorodiammino-platinum probably resulted from the decomposition of the Magnus's salt, the amine taking no part in the reaction.

Studies upon Catalytic Combustion.—Part I. The Union of Carbon Monoxide and Oxygen in Contact with a Gold Surface.

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Introduction.

The experiments which will be described in this and succeeding papers of the series are a continuation of the previous researches of Bone and Wheeler upon "The Combination of Hydrogen and Oxygen in Contact with Hot Surfaces," which were published in 1906.* They were begun at Manchester University twenty years ago, continued at the University of Leeds, and are now being completed at the Imperial College of Science and Technology, London. The delay in publishing the results has not been disadvantageous, because it has allowed of our testing some recent theoretical developments concerning catalytic combustion, and more particularly that due to Langmuir. These, it will be remembered, formed the subject of a special discussion held in London on September 20, 1921, under the auspices of the Faraday Society, in which a number of the leading investigators throughout the world participated.†

The previous work of Bone and Wheeler (*loc. cit.*), in which the actions of a number of widely different hot surfaces upon the combination of hydrogen and oxygen at pressures between 500 and 50 mm. were systematically studied, had disclosed the following outstanding facts:—

(1) That the catalyzing power of a new surface at a given temperature usually increases up to a certain steady "normal" state, after which the rate of steam formation is always directly proportional to the pressure, *provided that* the two gases (hydrogen and oxygen) are present in their combining ratios, and that the product (steam) is rapidly removed from the sphere of action.

(2) That, when one or other of the reacting gases is present in excess, the rate of combination is in most cases nearly proportional to the partial pressure of the hydrogen, which thus becomes the determining factor in any given experiment. This applied to such widely different surfaces as porcelain, magnesia, platinum, gold, nickel, calcined spathic iron ore (Fe_2O_3 plus MnO), and nickel oxide. Copper oxide, and to a certain extent also silver, proved

* 'Phil. Trans.,' A, vol. 206, pp. 1-67 (1906).

† 'Trans. Faraday Society,' vol. 17, pp. 546-675 (1922).

to be exceptional in this respect, inasmuch as the partial pressure of the oxygen, either generally or under certain definite conditions, became a governing factor.

(3) That, in conformity with the foregoing, the "normal" activity of most of the surfaces examined could be stimulated, often in a very high degree, by previous exposure to hydrogen at moderately high temperatures.

(4) That, in cases of surfaces composed either of readily oxidizable metals or of reducible oxides, the true catalytic combination of the gases does not involve any alternating oxidation and reduction of the surface, as many have supposed; indeed, it was shown that any such purely chemical view is quite inadequate to explain the phenomenon. Thus, in the case of copper oxide, the truly catalytic process was shown to depend primarily upon the condensation of a film of "activated" oxygen on the surface; indeed, so far from the CuO participating directly in the formation of steam, it was actually protected by the film of "activated" oxygen from the attacks of the hydrogen, which otherwise would have energetically reduced it.

The facts observed led to the conclusion that the real phenomenon of surface combustion "depends primarily on a condensation of one or other (and, in some cases, possibly both) of the reacting gases on the heated surface," and that the prime cause lies in an "activation" of the combining gases (certainly of the hydrogen and possibly also of the oxygen) by "association" with the surface, the question being left open whether such "association" is a mere surface "condensation" or some deeper "occlusion."

In a subsequent discussion upon the subject at the British Association in 1910, Sir J. J. Thomson suggested "that the action of surfaces might ultimately be found to depend on the fact that they formed a support for layers of electrified gas in which chemical changes proceed with high velocity."* Moreover, in 1914, Dr. Harold Hartley published an investigation on the electrical condition of an insulated gold or silver surface during the absorption of certain gases (hydrogen, carbon monoxide, or oxygen), and their catalytic combustion thereon, at a temperature of 275° C.,† in which it was shown (i) that the metal became *negatively* charged during the occlusion of either hydrogen or carbon monoxide, and *positively* so whilst occluding oxygen, (ii) that such charging of the metal was due to gas *leaving* rather than *entering* it. These significant observations seem to have escaped the attention of chemists who have subsequently studied the subject, but they must be reckoned with in any general

* 'Brit. Assoc. Reports,' 1910 (Sheffield).

† 'Roy. Soc. Proc.,' A, vol. 90, p. 61 (1914); also 'Trans. Inst. Gas Engineers,' p. 141 (1914).

theory of surface combustion. For, whilst they do not necessarily prove that the gases are, or must be, ionized before combustion, they are undoubtedly of importance as showing the inward and outward drift in respect of the zone of combustion at the surface.

In the year 1916 Langmuir published, in his well-known memoir upon the 'Constitution and Fundamental Properties of Solids and Liquids,'* a theory concerning chemical actions of surfaces (heterogeneous catalytic reactions) which included and developed further the basic ideas originally put forward by Bone and Wheeler. In the course of the said discussion at the Faraday Society he acknowledged that there were a great many statements in the Bone and Wheeler memoir of 1906 "which foreshadow in a general way some of the conclusions that we have reached more recently"; and in a subsequent private communication to one of us (W.A.B.) he admitted that "the general view-point which you had in 1906 was much ahead of others of that time, and is in many ways closely related to that which I have developed independently from a rather different experimental basis." Langmuir set out to apply to heterogeneous reactions and to the phenomena of adsorption and surface tension the new conception of crystal structure arising out of the work of W. H. and W. L. Bragg, and his speculative treatment of the subject has been highly suggestive and valuable. He agreed with Bone and Wheeler in identifying the well-known actions of hot surfaces in accelerating gaseous interactions with their powers of absorbing gases, although he used the term "adsorption" where they had used "absorption" or "occlusion." He further postulated that such "adsorption" is determined by chemical affinity, and that the adsorbed layers of gas are monomolecular in thickness, in which the molecules are definitely oriented.

In the private communication referred to Langmuir disclaimed "ever having looked upon ionization as the cause of activation in heterogeneous catalysis," saying that he had frequently made experiments to detect ionization in such cases, but without success. He thought, however, that "the electron emission may be changed by a reaction, but this is a purely secondary effect and cannot be regarded as the cause of chemical action, although both electron emission and chemical action may be modified by the presence of adsorbed films."

It may here be observed that in Langmuir's experiments upon the catalytic combustion of carbon monoxide (*loc. cit.*) the conditions were very different from ours. He heated a platinum wire electrically not only to higher temperatures, which in different experiments varied from "considerably

* 'Journ. Amer. Chem. Soc.,' vol. 38, pp. 2221-2295 (1916).

below red heat" up to white heat, but also in mixtures of carbon monoxide and oxygen at much lower pressures (*e.g.*, up to about 0.1 mm.) than those employed by us. In such circumstances he found at between 500° and 700° K the gases reacted at a rate directly proportional to the partial pressure of the oxygen and inversely to that of the carbon monoxide; within this range the reaction velocity increased rapidly with the temperature, about 1.6 fold for 10° at 600° K. Within a range of 750° to 1,050° K. the velocity was found to be independent of the temperature, being limited largely by the rate at which the gases can come into contact with the surface. At such temperatures, and with an excess of oxygen, the reaction velocity was proportional to the partial pressure of the carbon monoxide, while with an excess of the latter it was proportional to the partial pressure of the oxygen. Langmuir visualised the mechanism of the reaction as follows: Every oxygen molecule which strikes a *clean* platinum surface condenses upon it in the form of single atoms combined with separate platinum atoms, such chemical union being so firm that no appreciable evaporation of O atoms from the surface takes place even when the platinum is at 1,500° K. These "adsorbed" O atoms are in a very active condition in regard to their ability to react with the CO, and *every* CO molecule which strikes such an adsorbed O atom reacts with it to form CO₂. When CO molecules strike a clean platinum surface every one condenses on it, being held by chemical union between the C atoms and two platinum atoms. An adsorbed film of CO thus consists of a monomolecular layer of oriented molecules, which, however, are not so firmly held to the surface as are O atoms, because they evaporate at an appreciable rate at temperatures as low as 500° K. And because of their said orientation the adsorbed CO molecules are chemically very inert towards oxygen. At low temperature range the surface is nearly completely covered by such an oriented adsorbed CO film, and reaction only occurs when unadsorbed CO molecules from the inter-gaseous atmosphere strike O atoms which have become adsorbed in the spaces left vacant by the evaporation of condensed CO molecules. At high temperatures the surface is nearly covered with O, so that when there is excess of it present the reaction velocity is limited by the rate at which CO molecules strike the surface; on the other hand, when excess of CO is present, the surface is largely bare, and the reaction velocity is limited by the rate at which O₂ molecules strike the surface, because the oxygen remains on the surface in an atomic condition until struck by a CO molecule.*

* *Vide* 'Trans. Faraday Society,' *loc. cit.* pp. 653, 654.

It is important to note that the essential points in Langmuir's view are (1) that it is only the adsorbed oxygen which is really activated by the surface, whose function it is to atomize the O_2 molecules as they condense upon it; (2) that adsorbed CO molecules are not activated at all, but, on the contrary, are rendered chemically very inert towards oxygen, and by blanketing the surface as a monomolecular film act as a "poison" towards it; and (3) that CO_2 is only formed when an unadsorbed CO molecule from the surrounding atmosphere strikes "atomized" oxygen condensed on the surface. It may here be observed that in the course of experiments which will be detailed in this and succeeding papers much experimental evidence has been accumulated showing that catalytic combustion at such pressures as we have employed probably involves deeply occluded gases as well as merely "adsorbed" monomolecular films at the surface, and that the mechanism of the process is more complex than the Langmuir school suppose. Indeed, it seems to us hazardous to base a general theory of catalytic combustion solely or even principally upon experiments at such exceedingly low pressures as Langmuir employed; for it by no means follows that the order of things will be just the same at pressures of several hundreds of millimetres as it is at 0.1 millimetre.

It will be necessary also to deal at some length in a subsequent paper with the vitally important question as to whether or not moisture functions in any way (except mechanically) in the catalytic combustion of carbon monoxide, an aspect of the case which recent investigators seem to have overlooked. For if, as will then be shown, moisture probably *does* exert an influence which is not merely mechanical, the further question will arise what *rôle* does it play, and how far consequently some recent theories require to be modified.

Of late years there has been a disposition in some quarters to revive the old idea of de la Rive, which Faraday so strongly opposed in 1833-4, that catalytic combustion involves a rapidly alternating series of oxidations and reductions of the surface. All that need be said about it now is that, not only did Bone and Wheeler's work (*loc. cit.*) bring to light many facts which seem irreconcilable with this idea, but also that more such facts have been discovered during the progress of the present researches, which will in due course be detailed.

Two other recent contributions to the subject remain to be mentioned. D. L. Chapman* and his co-workers, whose experiments on the union of hydrogen and oxygen in presence of silver and gold confirmed the Bone-Wheeler effect, namely, that the "normal" activity of such surfaces can be stimulated by previous exposure to hydrogen, have suggested that it can be better explained

* 'Proceedings,' A, vol. 107, pp. 92-100 (1925).

on the supposition of the removal of inhibiting oxygen than on that of activation by absorbed hydrogen. Again, H. S. Taylor,* as the outcome of his Princeton studies, has concluded that some modification of the Langmuir concept is necessary, namely, in the sense that only a very small fraction of a catalysing surface is really active. There is doubtless a good deal of cumulative evidence, to which the experiments recorded herein have added, of catalysing surfaces being sensitive to heat treatment; but whether such evidence warrants the conclusion that the catalyst must be considered as composed of *active* and *inactive* particles, rather than as an assemblage of particles whose several activities may vary between zero and a maximum, is debatable. Both of these points have always been before us, and will be referred to again. Meanwhile, having regard to the complexity of the phenomena associated with catalytic actions, we will content ourselves with remarking how easily the most experienced workers may be misled by isolated or particular sets of observations, unless the actions of many different types of surfaces at various temperatures and pressures be studied and reviewed. Indeed, the dominant factors in one particular set of circumstances may be, and sometimes demonstrably are, different from those prevailing in another; and experience has made us sceptical about attempts to apply particular explanations comprehensively to *all* cases.

Before passing on to the experimental part of the work, we desire to direct attention to the importance, in recording results with any particular surface, of giving in outline a complete chronological account of them. Indeed, in interpreting any particular set of results, it is necessary always to take into account the previous history of the surface, and to follow most carefully any change in its catalytic power induced by special circumstances. For in our experience the certainty with which the surface can be restored to a "normal" state after a given change of condition is often a criterion of the value of a series of experiments. We would even go so far as to say that, unless this condition can be fulfilled (or its non-fulfilment simply explained) in a given series of experiments, their trustworthiness in relation to theoretical issues may be doubted. This rule will be carefully observed in detailing our experiences.

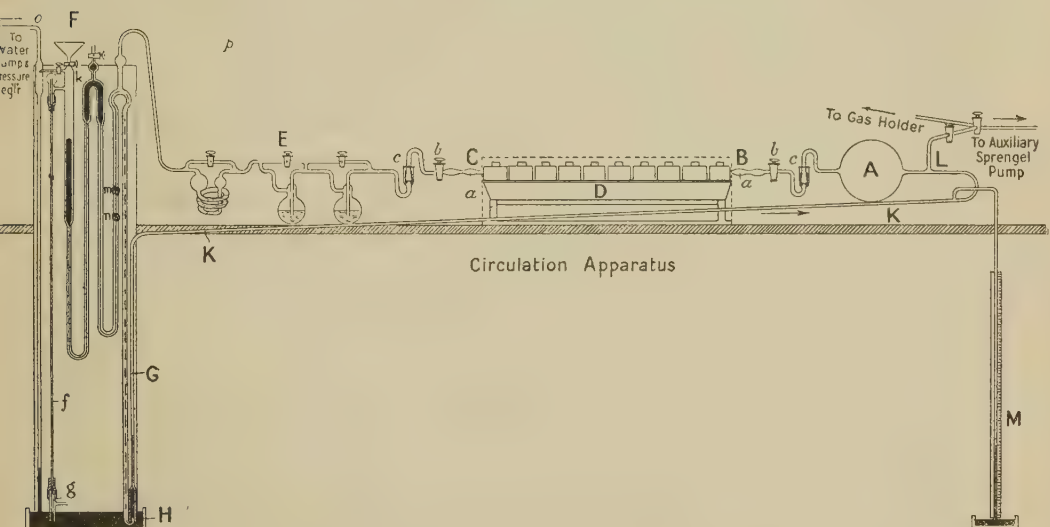
Apparatus and Experimental Method.

The experimental method employed throughout the investigation was in principle the same as that used by Bone and Wheeler. It consisted in circulating continuously in a closed system a homogeneous mixture of the reacting gases, at a uniform rate, over the particular surface under investigation. The

* *Ibid.*, vol. 108, pp. 105-111 (1925).

surface was maintained at a constant temperature, and absorption bulbs containing a solution of barium hydroxide were inserted in the circuit for the rapid removal of the reaction product. The rate of combination was always measured by observing the pressure in the apparatus at regular intervals of time.

The apparatus is shown in the accompanying diagram, in which the globe A (capacity = 1,200 c.cms.), containing a few c.cs. of distilled water, served as a reservoir for the reacting gases; D was a constant temperature furnace in which the Jena hard glass combustion tube BC, containing the surface under



examination, was heated; E was a series of bulbs containing a solution of baryta water for absorption of the carbon dioxide; whilst F was an automatic Sprengel pump employed for maintaining the circulation of the gases in the system. An auxiliary pump (not shown in the diagram) was employed, as and when required, for evacuating the apparatus between experiments. The manometer M served for pressure observations during an experiment. Each end of the combustion tube BC was fitted with special glass joints (*aa*), composed of rings of glass of gradually diminishing hardness fused together, ending ultimately in a grade of glass soft enough to allow of its being fused on to the mercury cup taps *bb*. The adoption of these special joints obviated the use of any india-rubber connections in the apparatus.

First Series of Experiments with Gold Gauze at 300° C.

Gold was selected as the first metallic surface to be examined on account of its non-oxidizable character and supposed indifference to carbon monoxide.

It was used in the form of a gauze of 22 strands (each 0.15 mm. in diameter) per centimetre, specially woven for us out of the purest wire obtainable by Messrs. Johnson and Matthey, to whom our best thanks are due. It had been employed in the previous work on hydrogen and oxygen, and weighed 52.5 grams, the surface exposed to the reacting gases being about 445 cm.²

In several respects the action of this metal proved to be one of the most interesting of all the surfaces investigated. For, in addition to its being one of the most active in promoting the gaseous combination, its catalysing power proved to be highly susceptible, not only to structural changes in the metal itself, but also to stimulation in a high degree by previous exposure to either of the reacting gases at the experimental temperature. Also, as will be shown later, its catalysing power seemed to be dependent on the presence of moisture in the system, a very remarkable result of deep theoretical significance. Taken as a whole, the results constitute a strong, if not irresistible, body of evidence that it is not merely superficially adsorbed gas which (as Langmuir has supposed) is activated by the metal, but that more deeply occluded gas plays an important *role* in the process.

We first of all made the following series of thirty-six experiments, extending over a continuous period of about two months. During the first seventeen of them (I to XVII) successive charges of a normal $2\text{CO} + \text{O}_2$ mixture, saturated with aqueous vapour at from 20 to 26° C., were circulated over the gauze at 300° C., until its catalysing power, which at first was sub-normal, had assumed a steady value. Incidentally, it was proved that no hydrogen was liberated (*e.g.*, as the result of interaction between CO and H_2O) at any time during the catalytic combustion. As soon as the aforesaid steady state had been established, three consecutive experiments (XVIII to XX) showed the proportionality of the rate of combination to the pressure of the dry nitrogen-free reacting mixture (P).

It should be noted that in all tabulated results included in this paper—

t = time in hours from the beginning of each experiment,

T = temperature of the catalysing surface in the combustion tube,

θ = the temperature of the moist gas in the main part of the apparatus,

P = corrected pressure of the nitrogen-free gaseous mixture in the apparatus,

P_{CO} & P_{O_2} = partial pressures of the CO and O_2 respectively in the apparatus,

k_1 = the velocity constant calculated from the equation of a reaction of a first order,

$$k_{CO} = \frac{1}{t} \log \frac{P_{CO}}{P_{tCO}}, \quad k_{O_2} = \frac{1}{t} \log \frac{P_{O_2}}{P_{tO_2}}.$$

The chronological sequence of the experiments is indicated by Roman numerals, near each of which is indicated, by means of an ordinary numeral in brackets, the day in the series on which the particular experiment was made. It should also be noted that in all cases the gaseous mixture employed was saturated with moisture at the temperature θ .

Experiments XVIII to XX with Mixture $2CO + O_2$ showing the Proportionality of the Reaction Velocity to the Pressure.

Expt.	XVIII (21) T = 298 to 304°. $\theta = 25^\circ$		XIX (22) T = 300 to 302°. $\theta = 25.7^\circ$		XX (23) T = 298°. $\theta = 25^\circ$	
t hours.	P mm.	k_1	P mm.	k_1	P mm.	K_1
0	399	—	368	—	430	—
$\frac{1}{2}$	288	0.2832	257	0.3102	315	0.2702
1	203	0.2935	184	0.3010	228	0.2756
$1\frac{1}{2}$	148	0.2872	136	0.2882	166	0.2756
2	108	0.2838	97	0.2895	119	0.2790
$2\frac{1}{2}$	76	0.2881	70	0.2883	84	0.2837

REMARKS.—This first steady state of the catalysing power of the surface, when k_1 varied between 0.275 and 0.310, corresponded to the disappearance of between 46 and 50 per cent. of the original mixture within the first hour.

Experiments showing the Stimulating Effect of Oxygen upon the Catalysing Power of the Surface.

On the day immediately following Experiment XX a charge of nearly equal volumes of the reacting gases ($CO + O_2$), saturated with moisture at $25^\circ C.$, was introduced into the apparatus, the rate of circulation remaining unaltered. The presence of excess oxygen was found to stimulate quite appreciably the metal's catalysing power, 60 per cent. of the original CO disappearing during the first hour; the rate of combination was as nearly as possible directly proportional to the partial pressure of the CO throughout the experiment, as shown below:—

Experiment XXI (25). $T = 300^\circ$. $\theta = 25^\circ$.

t hours.	P_{CO} mm.	P_{O_2} mm.	k_1CO	k_1O_2
0	191.3	198	—	—
1	77.5	141	0.3924	0.1475
$1\frac{1}{2}$	49.4	127	0.3926	0.1286
2	32.1	118	0.3876	0.1124
$2\frac{1}{2}$	20.3	112	0.3896	0.0989
3	14.1	109	0.3775	0.0864

REMARKS.—The surface was more active than before, as shown by the increased value k_1CO , which, however, remained nearly constant throughout the experiment.

Immediately afterwards the surface was left in contact with the residual oxygen (102 mm.) at 300° for a further period of 60 hours, whereupon, after exhausting the apparatus (two hours) and admitting a fresh charge of the normal mixture ($2CO + O_2$), the catalysing power of the metal was found to have been extraordinarily stimulated, as the following results show:—

Experiment XXII (28). Mixture $2CO + O_2$. $T = 300^\circ$. $\theta = 24^\circ$.

t	0	$\frac{1}{2}$	1	$1\frac{1}{2}$ hrs.
P	380	156	48	16 mm.
k_1	—	0.773	0.898	0.907

Such a result was unexpected, because in the previous investigation on the combination of hydrogen and oxygen over the same surface at $250^\circ C$. (*loc. cit.*, pp. 45 to 50) no stimulation by previous oxygen treatment had been observed. Moreover, in the present case it is noteworthy that *the full effect of the stimulus was not immediately apparent, but only became so after the lapse of half an hour*, a circumstance which was confirmed in subsequent experiments not here detailed.

In the next five experiments (XXIII to XXVII inclusive), the details of which need not be reproduced, successive charges of the normal mixture $2CO + O_2$ were circulated over the surface, during which its catalysing power gradually assumed another fairly steady value ($k_1 = 0.43$). This, however, was still decidedly higher than the previous normal rate (XVIII to XX), showing that the oxygen stimulus had not yet entirely disappeared. Then followed five more experiments (XXVIII to XXXII inclusive), with mixture originally containing excess of oxygen, in which the proportionality of the rate of combination to the partial pressure of the CO, and the stimulating effects of the oxygen treatment, were confirmed.

Experiments showing the Stimulating Effect of Carbon Monoxide upon the Catalysing Power of the Surface.

Having thus established the effects of excess oxygen, we were now ready to investigate those of excess of carbon monoxide; this was accordingly done in the next group of five experiments (XXXII to XXXVI inclusive), the results of which will be considered in detail in chronological order.

The surface having been got back again nearly to its true "normal" activity after the previous oxygen treatment ($k_1 = 0.2971$ for a mixture $2\text{CO} + \text{O}_2$ at the end of Experiment XXXI), a mixture $4\text{CO} + \text{O}_2$ was introduced into the apparatus (XXXII) with the following results, showing the rate of combination to be still strictly proportional to the partial pressure of the carbon monoxide, the surface being progressively stimulated by the excess of that gas as the experiment proceeded, as evidenced by the k_{O_2} values:—

Experiment XXXII (52). $T = 300^\circ$. $\theta = 23.5^\circ$.

t hours.	P_{CO} mm.	P_{O_2} mm.	k_{CO}	k_{O_2}
0	310	76	—	—
0.5	267	54	0.1300	0.2968
1	224	33	0.1412	0.3623
1.5	195	19	0.1343	0.4014
2	169	5	0.1317	0.5886

The residual CO (moist) was afterwards circulated over the surface at 300° for 24 hours, at the end of which a sample was withdrawn for analysis; it was found to contain no hydrogen, proving that under the experimental conditions no appreciable interaction between carbon monoxide and steam had occurred. The remainder of the CO was then kept circulating over the surface at 300° for a further 72 hours, when it was rapidly pumped out, and a charge of the normal mixture $2\text{CO} + \text{O}_2$ immediately introduced (XXXIII), with the following very significant results:—

Experiment XXXIII (56) with $2\text{CO} + \text{O}_2$ after CO Treatment followed by a Rapid Evacuation of the Surface. $T = 300^\circ$. $\theta = 21.4^\circ$.

t	0	$\frac{1}{4}$	$\frac{1}{2}$	1 hr.
P	398	307	170	42 mm.
k_1	—	0.4512	0.7390	0.9767

The apparatus was thereupon thoroughly exhausted for a period of 36 hours, the surface being maintained at 300° all the time, after which the foregoing experiment was repeated as follows :—

Experiment XXXIV (58) with $2\text{CO} + \text{O}_2$ after further Prolonged Exhaustion.

$$T = 300^{\circ}. \quad \theta = 22.2^{\circ}.$$

t	0	$\frac{1}{2}$	1	$1\frac{1}{2}$ hrs.
P.....	422	271	139	47 mm.
k_1	—	0.3846	0.4823	0.6355

It is thus seen that, not only were the stimulating effects of previously exposing the surface at the experimental temperature to either of the two reacting gases much the same, but also *the full extent of such stimulus was in neither case felt until some time after the system had recovered from the effects of the exhaustion to which it had been subjected immediately before such experiment.* This was especially manifest in Experiment XXXIV, where, after the prolonged exhaustion which immediately preceded it, the value of k during the first half-hour was 0.3846; during the next half-hour, as calculated for that particular interval, it rose to 0.58, whilst for the third half-hour it reached 0.9418. Presumably the effect of the prolonged exhaustion which immediately preceded the experiment would be to remove the greater part of the superficially adsorbed gas film, as well as some of the gas occluded near the surface, but very little of the more deeply occluded gas.

In order to test the matter further, at the conclusion of Experiment XXXIV the apparatus was again exhausted for one hour, and then another mixture with large excess of CO ($4\text{CO} + \text{O}_2$) was introduced (Experiment XXXV, 60th day), with results (not here detailed) confirming those of Experiment XXXII that the rate of combination in the system is proportional to the partial pressure of the CO. The residual moist CO (180 mm.) was afterwards circulated over the surface at 300° for 72 hours, and then the apparatus was exhausted as rapidly as possible, in such a manner that the reaction tube containing the surface was only subjected momentarily to the influence of the vacuum before the introduction of the next charge of normal mixture ($2\text{CO} + \text{O}_2$). The effect of such a procedure was shown to be as follows :—

Experiment XXXVI (63) with $2\text{CO} + \text{O}_2$ after CO Treatment followed by a

$$\text{Momentary Exhaustion. } T = 300^{\circ}. \quad \theta = 21.1^{\circ}.$$

t	0	$\frac{1}{2}$	1	$1\frac{1}{2}$ hrs.
P.....	418	126	62	25
k_1	—	1.0416	0.8288	0.8155

From a comparison between the result of Experiment XXXVI and those of Experiments XXXIII and XXXIV, it would appear that *the shorter the time during which the metal surface was exhausted after the CO treatment the sooner was the full stimulating effects of the latter upon the reaction of the CO-gold-O system realized.*

At the conclusion of this series the gold gauze was removed from the apparatus and examined microscopically, without, however, the least sign of "pitting" being discernible. The surface appeared to be just as smooth and bright as it was when the experiments were started; indeed, no visible change at all in its condition could be detected. The gauze was then replaced in the reaction tube of the apparatus in readiness for the next series of experiments, which were started after an interval of 21 days.

Second Series of Experiments. $T = 320^\circ$.

In this series of experiments, which extended altogether over a period of 56 days, it was discovered that the catalysing power of the metal could be greatly diminished either (a) by keeping it in a vacuum for many days at the room temperature, or (b) by a prolonged evacuation of it at the reaction temperature (320°).

The first of these effects was discovered by chance; for it so happened that at the end of the previous series of experiments the furnace used for heating the reaction tube had been turned out, without any other part of the apparatus being interfered with, because of the then approaching winter vacation. In this condition it remained for about 21 days, the gold gauze thus being kept all the time at the room temperature (10 to 15° C.) in the reaction tube of the apparatus, to which air had been admitted. At the end of this period the furnace was relighted and its temperature brought to 320° , the whole apparatus being evacuated meanwhile. On subsequently introducing a charge of the normal mixture ($2\text{CO} + \text{O}_2$), the reactivity of the surface was found to be extraordinarily feeble, although in course of time it gradually increased, as the following results show:—

Experiment XXXVII (1) with Mixture $2\text{CO} + \text{O}_2$. $T = 316$ to 318° .

$$\theta = 21.0.$$

t	0	1	2	3	$7\frac{1}{2}$	20 hours.
P.....	413	398	375	350	241	18 mm.
k_1	—	0.0161	0.0210	0.0239	0.0315	0.0680

This recovery of the catalysing power continued during the next two experiments (XXXVIII and XXXIX) until it finally attained a steady normal value, corresponding to $k_1 = 0.275$ as follows:—

Experiment XXXVIII (3). Mixture = $2\text{CO} + \text{O}_2$. $T = 320^\circ$. $\theta = 21.3^\circ$.

t	0	1	2	3	4	$5\frac{1}{2}$ hours.
P.....	438	359	294	219	157	86 mm.
k_1	—	0.0864	0.0866	0.100	0.111	0.129

Experiment XXXIX (9). Mixture = $2\text{CO} + \text{O}_2$. $T = 324^\circ$. $\theta = 21.0^\circ$.

t	0	1	2	3 hours.
P.....	321	171	93	48 mm.
k_1	—	0.273	0.269	0.275

The furnace was thereupon turned out, and the temperature of the gauze in the reaction tube thereby lowered to about 15°C . again, at which it was kept *in vacuo* for about eight days; whereupon the furnace was relighted and the temperature of the reaction tube quickly raised to 320° again, the apparatus being re-exhausted for an hour immediately before introducing the new charge of the gaseous mixture $2\text{CO} + \text{O}_2$ (Experiment XL). The following measurements then showed another great diminution in the catalysing power of the surface, consequent upon the prolonged reduction in its temperature.

Experiment XL. (17) Mixture = $2\text{CO} + \text{O}_2$. $T = 321$ to 323° . $\theta = 20.8^\circ$.

t	0	1	2	3	4	$9\frac{1}{2}$ hours.
P.....	407	361	322	283	246	105
k_1	—	0.0521	0.0508	0.0526	0.0547	0.062

It actually took about four days at 320° for the metal to recover its normal activity, but it eventually did so (Experiment XLI on 21st day), k_1 rising to 0.23 again. In a subsequent experiment (XLV on 46th day), after the surface had again been kept *in vacuo* at the room temperature for 10 days, it was once more reduced to 0.0496; and it was finally (Experiment XLVI) brought back nearly to the normal value ($k = 0.228$) after remaining at 320° for two days longer.

We think it highly probable that the alternate diminutions and restorations of the catalysing power of the surface recorded during the foregoing experiments were connected with slow structural changes in the metal itself. It

was indeed remarkable how, whenever the catalysing power had been enfeebled by the prolonged cooling of the metal at the room temperature, it was invariably slowly restored to as nearly as possible the same normal value when the temperature was raised to 320° again.

In another group of experiments (XLII to XLIV) it was proved that the catalysing power of the surface could also be diminished by prolonged evacuation at the experimental temperature (320° C.), though not to the same degree as by keeping it at the room temperature for a similar period (*c.f.* Experiments XXXVII and XL). Thus, after Experiment XLI, during which the surface had recovered its normal activity, the reaction tube containing it was kept continuously evacuated for a week without any reduction in temperature. The result of this treatment was a marked diminution in its catalysing power, as the following Experiment shows :—

Experiment XLII (29). Mixture $2\text{CO} + \text{O}_2$. $T = 320^{\circ}$. $\theta = 20^{\circ}$.

t	0	$\frac{1}{4}$	$\frac{1}{2}$	1	2	4	7 hrs.
P.....	425	403	374	325	247	135	52 mm.
k_1	—	0.092	0.111	0.116	0.118	0.124	0.130

How exceedingly slow was the re-attainment of normal catalysing power after the aforesaid prolonged evacuation may be judged from the following summarized results, which again indicate that not merely superficially “adsorbed” but also more deeply occluded gas was involved.

Experiment.	Duration Hours.	k_1		
		1st Hour.	At End.	
XLIII (30)	5	0.128	0.152	Mixture. $2\text{CO} + \text{O}_2$ $T = 320^{\circ}$ $\theta = 20^{\circ}$
XLIV (31)	$4\frac{1}{2}$	0.145	0.205	

At the conclusion of this series the surface, having been brought back again nearly to its “normal” condition of activity ($k = 0.228$ for a mixture $2\text{CO} + \text{O}_2$ in Experiment XLVI on the 48th day), it was thought desirable to test once more its responsiveness to an excess CO treatment. Accordingly, on the 53rd day, a mixture originally corresponding to $4\text{CO} + \text{O}_2$ was admitted to the apparatus, which had just previously been continuously exhausted for 12 hours, with the following highly interesting results :—

Experiment XLVII (53). $T = 316$ to 320° . $\theta = 23^\circ$.

t hours.	P_{CO} mm.	P_{O_2} mm.	k_{CO}	k_{O_2}
0	346.0	86.9	—	—
1	249.5	38.6	0.142	0.35
2	186.0	6.6	0.135	0.59
x	172.5	nil	—	—

The residual 172 mm. of CO were thereupon kept circulating over the surface at 320° for three days longer, and then rapidly pumped out. On admitting a "normal" $2\text{CO} + \text{O}_2$ mixture, the catalysing power of the surface was found to have been extraordinarily stimulated by the long CO treatment, as the following results show:—

Experiment XLVIII (56) with Mixture $2\text{CO} + \text{O}_2$. $T = 320^\circ$. $\theta = 20.2^\circ$.

t	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$ hr.
P.....	392	319	241	180	132	62 mm.
k_1	—	1.074	1.267	1.352	1.418	1.602

Not only was the powerful stimulating effect of CO upon the surface once more strongly demonstrated, but also it was again proved that the *full effect of such stimulus was not immediately felt*, all of which points to the potent influence of deeply occluded, as distinct from merely adsorbed, gas in the process. Moreover, the stimulus so imparted to the metal by the CO treatment was very long enduring.

Third Series. $T = 275^\circ$.

In a final series of experiments, extending over 35 days, in which the temperature of the reaction tube was lowered to 275°C. , the previous results were generally confirmed. The k_1 value for a mixture of $2\text{CO} + \text{O}_2$ with the surface in a "normal" condition of activity was now as nearly as possible 0.100. Under the stimulating influence of prolonged O_2 treatment it rose to 0.15. When a mixture corresponding to $4\text{CO} + \text{O}_2$ was introduced into the apparatus, there was an immediate great stimulation of the activity of the surface (the k_{O_2} values, beginning at 0.25 rose to 0.52 at the end), the rate of combination being nearly proportional to the partial pressure of the CO ($k_{\text{CO}} = 0.114$ to 0.102). After the residual CO had been circulated over the surface at 275° for two days, and then withdrawn, its catalysing power was again found to be extraordinarily high, the k_1 value for the normal

$2\text{CO} + \text{O}_2$ mixture having risen to 1.28. Finally, the surface was subjected to a prolonged exhaustion for 10 days, after which its catalysing power at 275° was found almost to have vanished, and even when the temperature was raised to 320° the value of k_1 for a normal $2\text{CO} + \text{O}_2$ mixture was no higher than 0.010.

Summary.

Leaving the experimental proof of the dependence of the catalytic combustion of carbon monoxide, in contact with gold and silver, upon the presence of moisture in the system to be detailed in a subsequent paper, the principal facts established by the experiments described herein may be summarized as follows :—

(1) The rate of combination of a (moist) theoretical mixture of carbon monoxide and oxygen ($2\text{CO} + \text{O}_2$) in contact with a gold surface in a “normal” state of activity at 300°C. , or thereabouts, is always directly proportional to the pressure of the nitrogen-free mixture.

(2) The “normal” catalysing power of the surface at such temperature may be greatly diminished by *either* (i) cooling it down to, and keeping it for some time at, the ordinary room temperature, *or* (ii) prolonged evacuation of it without any such cooling.

(3) The re-attainment of “normal” activity by a surface whose catalysing power has been enfeebled by such treatments as the aforesaid is a slow process, usually extending over many hours.

(4) The catalysing power of the surface, when in “normal” activity, can be highly stimulated by previous exposure to *either* carbon monoxide *or* oxygen at the said experimental temperature; in neither case, however, was the full extent of such stimulus immediately manifested when the stimulating gas was rapidly removed and a fresh charge of the reacting mixture ($2\text{CO} + \text{O}_2$) re-introduced into the apparatus.

(5) Whenever, starting with the surface in a state of “normal” activity, either of the two reacting gases was originally present in excess, the subsequent rate of combination, which rapidly became super-normal, was always proportional to the partial pressure of the carbon monoxide, which thus became the controlling factor in such an experiment.

(6) Although the catalytic combustion was subsequently found to depend on the presence of moisture in the system, no hydrogen was ever detected in the reacting gases, even when a large excess of carbon monoxide was present.

(7) A microscopic examination of the gold surface at the conclusion of the experiments failed to reveal any signs of “pitting” having occurred; on the

contrary, neither the lustre nor the smoothness of the metal seemed to have suffered any diminution.

We think that such results are best explained on the supposition of an "activation" of *both* of the combining gases by association with the surface, and that such activation was by no means confined to superficially "adsorbed" gas-films of monomolecular thickness, but extended also to more deeply occluded gases. They also suggest that structural changes in the metal itself, or may be such changes in conjunction with deeply occluded gas, play an important part in the phenomena.

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Some Theoretical Calculations of the Physical Properties of Certain Crystals.

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§ 1. *Introduction.*

This paper is a continuation of a series of others, recently published,† in which an attempt is made to co-ordinate kinetic theory data with crystal

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† J. E. Jones, 'Roy. Soc. Proc.,' A, vol. 106, p. 441 (1924); 'Roy. Soc. Proc.,' A, vol. 106, p. 463 (1924); 'Roy. Soc. Proc.,' A, vol. 106, p. 709 (1924); 'Roy. Soc. Proc.,' A, vol. 107, p. 157 (1925). J. E. Jones and A. E. Ingham, 'Roy. Soc. Proc.,' A, vol. 107, p. 636 (1925). These papers will be referred to below as Papers I, II, III, IV and V respectively.

data simultaneously to determine interatomic fields. The methods there described are here elaborated and extended, and new considerations are introduced which have the effect of modifying the conclusions previously reached. The repulsive fields of a number of ions are determined and are used to calculate a number of crystal properties, including compressibility and elasticity, which are compared where possible with experiment. The calculations have been made as extensive as possible in order to explore to the full the possibilities of the central field of force and in particular that of the inverse power law.

The main features of the preceding papers were (i) the determination from certain gaseous properties of neon and argon of a series of models to represent their interatomic fields; (ii) the assumption of the equivalence of the repulsive fields of atomic or ionic cores of the same structure (*i.e.*, Cl^- and K^+ were assumed equivalent to A); (iii) the unique determination of the fields by a comparison of calculated and observed interatomic distances in the crystals NaF and KCl.

This method bears an apparent, though not a real, resemblance to one used earlier by Wasastjerna.* His work also falls into three natural stages. In the first he deduced from his previous work on ionic refractivities† the relative sizes of several groups of ions: for example, of the neon-like and argon-like ions—undoubtedly an interesting and valuable piece of information.

In the second stage he considered the forces between pure gas atoms. He assumed the repulsion to be according to an inverse power law and in particular to be that of the inverse 9th power. He then, somewhat inconsistently, assumed the atom to be a rigid sphere of known dimensions, and assumed the validity of van der Waal's equation. By the use of this equation at the critical temperature (where, in fact, it ceases to hold), an expression was obtained for the force constant of the gas in terms of its diameter and its critical data.

In the third stage the results were applied to crystals. Calculations were made of the size of a hypothetical cubic crystal of pure gas atoms, to which were added alternately positive and negative charges, using the force constant previously obtained. The atoms were then regarded as kations and anions respectively, and the calculated interatomic distance was apportioned between them according to their respective sizes as determined from their refractivities. The lengths so obtained were taken to be characteristic radii of the ions, invariable from crystal to crystal.

* Wasastjerna, 'Soc. Scientiarum Fenn. Com., Phys. Math.,' vol. 1, p. 38.

† Wasastjerna, *loc. cit.*, vol. 1, p. 37.

This division of the calculated interatomic distance is, however, somewhat arbitrary, for it is a function not only of the repulsive forces but also of the electrostatic forces. It is the repulsive force constants of the ions, which alone are characteristic, and these the method does not determine.*

The new feature of this paper is an attempt to determine these characteristic force constants. This is done by incorporating into the methods of the preceding papers† a modification to take into account Wasastjerna's results on ionic refractivities. The investigation indicates that the repulsive forces of the neon-like ions in crystals can be represented by an inverse 11th-power law, each ion having its appropriate force constant, while the repulsive forces of the argon-like ions can be represented by an inverse 9th-power law. This is in close accord with the power laws obtained by Born and Landé‡ in their simple deduction of repulsive fields from crystal compressibilities. A table has been drawn up exhibiting the forces between various ions. This is intended to give a truer representation of ionic fields than has yet been given, and to replace to some extent (for theoretical purposes) the characteristic *sizes* of ions as given by various writers.§

The forces determined in this paper are found to be singularly successful in explaining observed interatomic distances in crystals, and are shown to lead to values of crystal energies and compressibilities which are in satisfactory agreement with observation. The same forces are used to calculate a number of other crystal properties, but there is a shortage of experimental results with which to compare them. A further application can be made to predict the interatomic distances of crystals not yet measured. CaCl_2 is considered as an example.

Finally, the properties of crystalline argon are considered in some detail, and the conclusion is reached that, while an argon-like core appears to repel according to an inverse 9th power at small distances, a repulsion according to an inverse 15th power is more appropriate at large distances. A law of force is suggested which approximates to these laws at small and large distances.

* The difficulty becomes apparent in considering a crystal like CaF_2 , where there is proximity between two F ions. The force between these is now repulsive electrostatically as well as intrinsically, and cannot be represented by a "size" obtained from heteropolar combinations.

† Papers I-IV.

‡ Born and Landé, 'Verhandl. d. Deut. Phys. Gesell.,' vol. 20, p. 210 (1918).

§ Bragg, 'Phil. Mag.,' vol. 40, p. 169 (1920). Wyckoff, 'Proc. Nat. Acad. Sc.,' vol. 9, p. 33 (1923). Davey, 'Phys. Rev., N.S.,' vol. 18, p. 102 (1921). Wasastjerna, *loc. cit.* Bragg, 'Solvay Conference Report,' April, 1925.

No attempt is made in this paper to explain on theoretical grounds the conclusions reached regarding the laws of force. Attempts have been made by other writers* to find on the basis of simple atomic models the forces between atoms. It is interesting to find that the results obtained make plausible the laws of force found to be operative in crystals by the method of this paper.

§ 2. *The Force Constants of Ions.*

In a series of papers Wasastjerna† has deduced from the refractive indices of crystals and salts the refractivities of a number of atoms and ions. From these he has deduced on certain plausible assumptions the relative sizes of atoms and ions of similar electronic structure, as given in Table I.

Table I.—The Relative Sizes of Ions and Atoms.

$\rho^{--}/\rho.$	$\rho^{-}/\rho.$	$\rho/\rho.$	$\rho^{+}/\rho.$	$\rho^{++}/\rho.$
O ⁻⁻ 1.445	F ⁻ 1.240	Ne 1.00	Na ⁺ 0.938	Mg ⁺⁺ 0.817
S ⁻⁻ 1.386	Cl ⁻ 1.205	A 1.00	K ⁺ 0.912	Ca ⁺⁺ 0.838

The term “size” in the case of dynamical systems like the Bohr atom requires careful definition. Presumably the ratios obtained by Wasastjerna refer to the average distance of the outer electronic orbits from the nucleus, the distances depending on the effective nuclear charge. Now the forces called into play in an encounter between these atomic systems will clearly depend on the size of the outer orbits, and so, when the forces are represented by hard impenetrable shells, as they often are in applications of the kinetic theory, the dimensions of the shell may be regarded as directly proportional to the scale of the outer orbits. It is the variation of the latter among ions of the same electronic structure which Wasastjerna deduces from his refractivity results. The presumption is that the same figures give the variation of the kinetic-theory diameters, and so, if one is known (say that of the pure gas), the others may be deduced. Thus in Table II are given the values deduced from the results of a recent investigation by one of the present authors.‡

* Cf. Born, ‘Atomtheorie des festen Zustandes,’ 2nd edit. (1923), §38.

† Wasastjerna, ‘Soc. Scient. Fenn., Comm. Phys. Math.,’ vol. 1, p. 38.

‡ Paper II, p. 477; Paper IV, p. 168 (Table VI).

Table II.—The Diameters of Ions and Atoms (in Ångstrom units).*

0 ⁻ .	F ⁻ .	Ne.	Na ⁺ .	Mg ⁺⁺ .
3.40	2.92	2.35	2.20	1.92
S ⁻ .	Cl ⁻ .	A.	K ⁺ .	Ca ⁺⁺ .
4.34	3.77	3.13	2.86	2.62

The representation of repulsive fields by a rigid sphere is, however, quite inadequate for most purposes. For instance, if crystals consisted of a collection of ions of this nature, they would, in fact, be incompressible, a result which is contrary to experience. In the papers already referred to it was shown that a better representation of the force is an inverse power law.

For each assumed power law the application of the theory to certain gaseous properties of neon and argon gave the appropriate value of the force constant. A number of these values are given in Table III.† The symbol n refers to the index of the repulsive power law ($\lambda_n r^{-n}$).

Table III.—The Repulsive Force Constants of Neon and Argon.

n .	Neon.	Argon.
∞	0	0
21	$3.892 \cdot 10^{-165}$	$2.338 \cdot 10^{-162}$
15	$1.764 \cdot 10^{-119}$	$1.721 \cdot 10^{-117}$
11	$4.446 \cdot 10^{-89}$	$1.306 \cdot 10^{-87}$
9	$6.663 \cdot 10^{-74}$	$1.009 \cdot 10^{-72}$

The significance of the force constants is made more intelligible by the figure, which represents the potential function $\phi \left(-\frac{\lambda}{(n-1)} r^{-n+1} \right)$ drawn to scale for neon.

The rigid sphere model, represented by the straight lines AB and BC, is clearly the limiting case of the series of curves corresponding to inverse-power laws

* The dimensions here given refer to the "kinetic-theory" sizes, and are a measure of the *repulsive* field alone. They are not to be confused or compared with the sizes of ions given by other authors from crystal considerations alone (Bragg, Wasastjerna, etc., *loc. cit.*), where the effect of the electrostatic field is mixed up with that of the repulsive field.

† Paper II, p. 477; Paper III, p. 718; Paper IV, p. 168. This opportunity may be taken of pointing out a misprint in the table on p. 477, Paper II. The value of σ appropriate to $n = 9$ should read 7.053 and not 7.530. The force constants of Argon are taken from the investigation of the equation of state (Paper II), in preference to those obtained from viscosity (Paper I). The only justification for this lies in the measure of success attained. Calculations of crystal interatomic distances from the viscosity results yield values in all cases too small.

for various values of n . It represents the case of $n = \infty$. The distance OB is the diameter of the atom as deduced from the kinetic theory.*

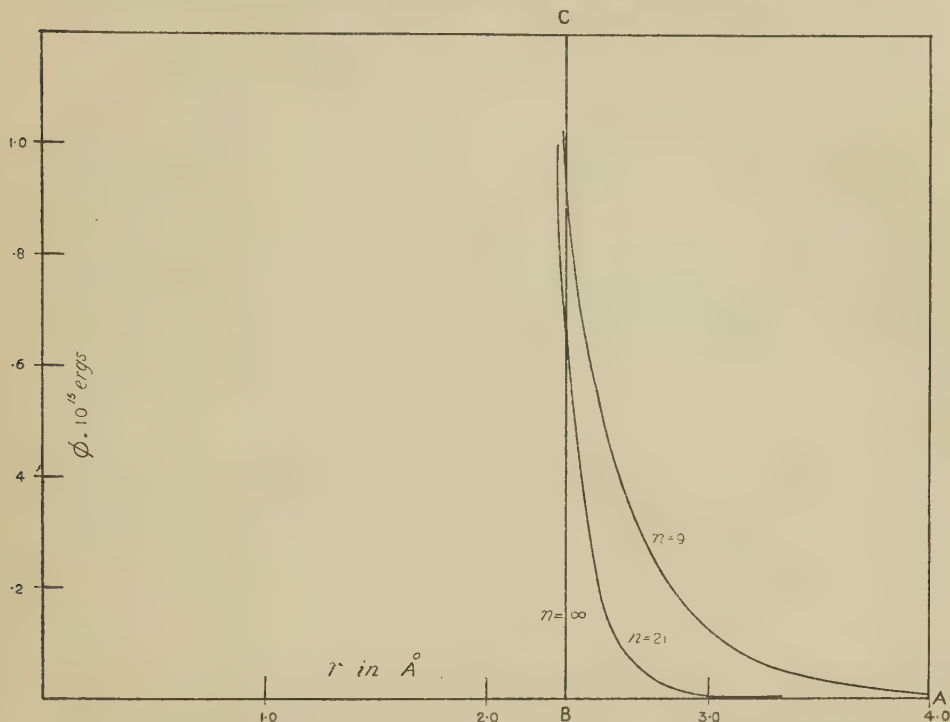


FIG. 1.—The Potential between two Neon Atoms for various Atomic Models ($\lambda_n r^{-n}$, $n = 9, 21$ and ∞).

The idea of a diameter can be generalised by considering the intersection of an ordinate of arbitrary value W with the series of curves, giving values PQ_n and $PQ_{n_2}, \dots, PQ_\infty$. The distance PQ_∞ represents the diameter of the atom as usually understood. In this paper we shall refer to each of the distances PQ_n as a “diameter,” and shall denote it by $\sigma^{(n)}$ to indicate that it is a function of n . The arbitrary ordinate W determines the scale on which the diameters $\sigma^{(n)}$ are measured. For any given value of W we have

$$PQ_n = \sigma^{(n)} = \left[\frac{\lambda_n}{(n-1)W} \right]^{1/(n-1)}, \quad (2.01)$$

and therefore

$$PQ_\infty = \sigma^{(\infty)} = \lim_{n \rightarrow \infty} \sigma^{(n)} = \lim_{n \rightarrow \infty} \left[\frac{\lambda_n}{(n-1)W} \right]^{1/(n-1)}. \quad (2.02)$$

For the purposes of this paper, the particular scale of the “diameters”

* Paper IV, Table VI, p. 168.

does not matter, but, in conformity with the work of the preceding papers,* the value of W is taken to be the average kinetic energy of an atom at 1° absolute, viz. $W = 3kT/2$, so that

$$\sigma^{(n)} = \left(\frac{\lambda_n}{2 \cdot 06 \cdot 10^{-16} (n-1)} \right)^{1/(n-1)}.$$

The assumption is now made that the "diameter" $\sigma^{(n)}$ is proportional to the scale of the outer orbits of the atom or ion and so can be dealt with in exactly the same way in which $\sigma^{(\infty)}$ was used to obtain Table II. We can thus deduce the value of $\sigma^{(n)}$ for an ion from that of an atom by using Wasastjerna's figures, quoted in Table I. This at once leads to a method of passing from the force constants of an atom to those of an ion, for

$$\sigma_+^{(n)} = \frac{\rho_+}{\rho} \sigma^{(n)},$$

and so

$$\left[\frac{\lambda_n^+}{(n-1)W} \right]^{1/(n-1)} = \frac{\rho_+}{\rho} \left[\frac{\lambda_n}{(n-1)W} \right]^{1/(n-1)}, \quad (2.03)$$

with the result that

$$\lambda_n^+ = \left(\frac{\rho_+}{\rho} \right)^{n-1} \lambda_n. \quad (2.04)$$

This result, be it noted, is independent of the choice of W .

From the figures given in Tables I and III we can now construct a series of force constants for each of the eight ions O^{--} , F^- , Na^+ , Mg^{++} , S^{--} , Cl^- , K^+ , and Ca^{++} . The results for the monovalent ions are given in Table IV.

Table IV.—The Repulsive Force Constants of Ions (force in dynes).

n	F^-	Na^+	Cl^-	K^+
21	$2 \cdot 872 \cdot 10^{-168}$	$1 \cdot 081 \cdot 10^{-165}$	$9 \cdot 66 \cdot 10^{-161}$	$3 \cdot 71 \cdot 10^{-163}$
15	$3 \cdot 582 \cdot 10^{-118}$	$7 \cdot 199 \cdot 10^{-120}$	$2 \cdot 32 \cdot 10^{-116}$	$4 \cdot 70 \cdot 10^{-118}$
11	$3 \cdot 819 \cdot 10^{-88}$	$2 \cdot 344 \cdot 10^{-89}$	$8 \cdot 37 \cdot 10^{-87}$	$5 \cdot 22 \cdot 10^{-88}$
9	$3 \cdot 723 \cdot 10^{-73}$	$3 \cdot 993 \cdot 10^{-74}$	$4 \cdot 478 \cdot 10^{-72}$	$4 \cdot 829 \cdot 10^{-73}$

The relative magnitudes of the force constants are seen more clearly if we choose such units for λ_n as will give the force in dynes when the unit of distance is the Ångström. These are given in Table V.

* Paper I, p. 452, *et seq.*

Table V.—The Repulsive Force Constants of Ions.

(The force in dynes when unit of length is Å.)

<i>n.</i>	F ⁻ .	Na ⁺ .	Cl ⁻ .	K ⁺ .
21	2·872 . 10 ⁵	1·081 . 10 ³	9·66 . 10 ⁷	3·71 . 10 ⁵
15	3·582 . 10 ³	7·199	2·32 . 10 ⁴	4·70 . 10 ²
11	3·819	0·234	83·7	5·22
9	0·372	0·040	4·478	0·483

We have now to investigate which of these series of models is the correct one, and, for this purpose, we make theoretical calculations of interatomic distances in crystals and compare the results with observation.

We shall, however, require not only the repulsive force between the kations and that between the anions, but also that between kations and anions. Now, if the fields of the ions *could* be represented by infinitely hard spheres, so that the field between positive ions was represented by spheres of diameter σ_{11} and that between negative ions by σ_{22} , then the force between positive and negative would be represented by a distance σ_{12} given by

$$\sigma_{12} = \frac{1}{2} (\sigma_{11} + \sigma_{22}).$$

Whatever be the correct method of obtaining from the force constants λ_{11} and λ_{22} a force constant λ_{12} appropriate to the interaction of positive and negative ions, it must, in the limit for infinite values of *n*, reduce to the law given above. We propose therefore to assume the validity of the law

$$\sigma_{12}^{(n)} = \frac{1}{2} (\sigma_{11}^{(n)} + \sigma_{22}^{(n)}),$$

the simplest assumption which satisfies this condition. We then get the formula

$$\lambda_{12}^{1/(n-1)} = \frac{1}{2} (\lambda_{11}^{1/(n-1)} + \lambda_{22}^{1/(n-1)}), \quad (2.05)$$

a result which is again independent of *W*.

The values thus obtained for the force constants between Na⁺ and F⁻ and that between K⁺ and Cl⁻ are given in Table VA.

Table VA.—The Forces between Anions and Kations.

<i>n.</i>	Na ⁺ ↔ F ⁻ .	K ⁺ ↔ Cl ⁻ .	Mg ⁺⁺ ↔ O ⁻⁻ .	Ca ⁺⁺ ↔ S ⁻⁻ .
21	2·142 . 10 ⁴	7·10 . 10 ⁶	4·559 . 10 ⁴	1·88 . 10 ⁷
15	5·837 . 10	3·77 . 10 ³	9·904 . 10	7·59 . 10 ³
11	1·047	2·30 . 10	1·527	3·76 . 10
9	0·1321	1·589	0·1787	2·36

§ 3. *The Determination of the Ionic Models.*

With the values of the force constants given in Table IV, it is now possible to make a series of calculations of the distances one would expect to find between ions in the crystals NaF and KCl (assumed to be face-centred cubics in accordance with observation). The attraction between ions is taken to be that due to their electrostatic charges.

The unit cell of a crystal of the rock-salt type is determined by three vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ where*

$$\mathbf{a}_1 = r_0 (\mathbf{i}_2 + \mathbf{i}_3), \quad \mathbf{a}_2 = r_0 (\mathbf{i}_3 + \mathbf{i}_1), \quad \mathbf{a}_3 = r_0 (\mathbf{i}_1 + \mathbf{i}_2), \quad (3.01)$$

r_0 being the closest distance between atoms and $\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3$ unit vectors parallel to the edges of the cube. Each cell contains one positive and one negative ion, their position in the cell being defined by

$$\mathbf{r}_1 = 0, \quad \mathbf{r}_2 = r_0 (\mathbf{i}_1 + \mathbf{i}_2 + \mathbf{i}_3) = \frac{1}{2} (\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3). \quad (3.02)$$

If $\phi^{(n)}$ and $\phi^{(e)}$ denote the contribution to the potential ϕ of one cell due to the repulsive and electrostatic forces respectively of all the other ions of an infinite crystal, we have

$$\phi = \phi^{(n)} + \phi^{(e)}, \quad (3.03)$$

and in the notation of a former paper†

$$\phi^{(n)} = \frac{(\lambda_{11} + \lambda_{22}) A''_{n-1} + 2\lambda_{12} A'_{n-1}}{(n-1) r_0^{n-1}}, \quad (3.04)$$

while‡

$$\phi^{(e)} = -\frac{3 \cdot 495 e^2 z^2}{r_0}, \quad (3.05)$$

e being the electrostatic charge and z the valency.

The total potential energy of N cells is then given by

$$\Phi = \frac{N}{2} \phi, \quad (3.06)$$

while the work required to separate to infinity the individual ions of the N cells is

$$U = -\Phi = -\frac{N}{2} \phi. \quad (3.07)$$

The condition that Φ shall be a minimum leads to

$$r_0^{n-2} = \frac{(\lambda_{11} + \lambda_{22}) A''_{n-1} + 2\lambda_{12} A'_{n-1}}{(3 \cdot 495) e^2 z^2}, \quad (3.08)$$

* Born, *loc. cit.*, p. 566.

† Paper V, *loc. cit.*

‡ Emersleben, 'Phys. Ztschr.', vol. 24, pp. 73 and 97 (1923). Born, *loc. cit.*, p. 733.

and so, for the series of force constants given in Tables IV, V and VA, we get a series of values of r_0 for the crystals NaF and KCl. These are produced in Table VI, and a comparison with the observed values indicates that the neon-like ions repel according to an inverse 11th power of the distance, while the argon-like ions repel according to an inverse 9th power.

Table VI.—Calculated and Observed Interatomic Distances in NaF and KCl.

n .	∞ .	21.	15.	11.	9.	Obs.
NaF	2.56	2.49	2.41	2.30	2.20	2.310 (*)
KCl.....	3.32	3.37	3.32	3.24	3.13	3.138 (*)

(*) W. P. Davey, 'Phys. Rev.,' vol. 21, 2, p. 143 (1923), W. H. Bragg and W. L. Bragg, 'X-rays and Crystal Structure,' 4th Edition, p. 306 (1924).

These results can be tested by calculating without further assumption the interatomic distances of the divalent crystals MgO and CaS. By the use of the appropriate values of λ_{11} , λ_{22} and λ_{12} for $n = 11$ and $n = 9$ respectively in the two cases, we arrive at the results given in Table VII.*

Table VII.—Calculated and Observed Interatomic Distances in MgO and CaS.

Crystal.	Calc.	Obs.
Mg O	2.10	2.09 (*)
Ca S	2.77	2.77 (†)

(*) R. W. G. Wyckoff, 'Amer. J. Sci.,' series 5, vol. 201, p. 138 (1921). Bragg and Bragg, *loc. cit.*, p. 300.

(†) W. L. Bragg, 'Phil. Mag.,' vol. 40, p. 181 (1920). Bragg and Bragg, 'X-rays and Crystal Structure,' give a value 2.82, p. 166.

To show how the calculated distance depends on the ionic model in these cases, the values appropriate to all the models are reproduced in Table VIII. The calculated distance is seen to be sensitive to changes in the value of n .

Table VIII.—The Dependence of the Calculated Interatomic Distance in MgO and CaS on the Value of n .

n .	21	15	11	9
MgO	2.45	2.29	2.10	1.93
CaS	3.31	3.18	2.98	2.77

* The force constants for O^{--} and Mg^{++} for $n = 11$ are 17.66 and 0.0589 respectively; those of S^{--} and Ce^{++} for $n = 9$ are 13.75 and 0.2452; other force constants are given in Table VA.

§ 4. *The Repulsive Forces Between Ions.*

In order to deal with crystals like NaCl we require a knowledge of the interaction between neon-like and argon-like ions. As the one set of ions repel each other according to an inverse 11th and the other set according to an inverse 9th power law, it seems reasonable to *assume* that the force between one of each type is according to an inverse 10th power law.

The method we suggest for finding the force constant is to plot the "diameters" $\sigma^{(n)}$ of neon and argon as a function of n (or more conveniently as a function of $1/n$) and to deduce by interpolation the value of $\sigma^{(n)}$ for $n = 10$. We can then write, as before,

$$\sigma_{12}^{(n)} = \frac{1}{2} (\sigma_{11}^{(n)} + \sigma_{22}^{(n)}),$$

a relation true for $n = \infty$, but empirical for other values of n . The appropriate values of the force constants are then obtained as before.

The method cannot claim strict accuracy, for interpolation in $\sigma^{(n)}$ may be in error by 0.5 per cent., causing errors in $\lambda_{12}^{(n)}$ of the order of 5 per cent. In those applications where $\lambda_n^{\frac{1}{n-1}}$ is used, as in calculations of interatomic distances, the order of accuracy is the same as that of $\sigma^{(n)}$.

Table IX.—The Repulsive Forces between Monovalent Ions at a Distance of 1 Å apart (in dynes).

	F ⁻ .	Na ⁺ .	Cl ⁻ .	K ⁺ .
F ⁻	3.82 ($n = 11$)	1.05 ($n = 11$)	5.955 ($n = 10$)	1.37 ($n = 10$)
Na ⁺	1.05 ($n = 11$)	0.234 ($n = 11$)	2.01 ($n = 10$)	0.484 ($n = 10$)
Cl ⁻	5.955 ($n = 10$)	2.01 ($n = 10$)	4.48 ($n = 9$)	1.59 ($n = 9$)
K ⁺	1.37 ($n = 10$)	0.484 ($n = 10$)	1.59 ($n = 9$)	0.483 ($n = 9$)

By applications of this method it is possible to draw up lists of force constants such as those of Tables IX and X, exhibiting the forces between any two ions of the series.

Table X.—The Repulsive Forces between Divalent Ions at a Distance of 1 Å apart (in dynes).

	O ²⁻ .	Mg ²⁺ .	S ²⁻ .	Ca ²⁺ .
O ²⁻	17.66 (<i>n</i> = 11)	1.53 (<i>n</i> = 11)	22.07 (<i>n</i> = 10)	1.95 (<i>n</i> = 10)
Mg ²⁺	1.53 (<i>n</i> = 11)	0.059 (<i>n</i> = 11)	3.14 (<i>n</i> = 10)	0.185 (<i>n</i> = 10)
S ²⁻	22.07 (<i>n</i> = 10)	3.14 (<i>n</i> = 10)	13.75 (<i>n</i> = 9)	2.36 (<i>n</i> = 9)
Ca ²⁺	1.95 (<i>n</i> = 10)	0.185 (<i>n</i> = 10)	2.36 (<i>n</i> = 9)	0.245 (<i>n</i> = 9)

§ 5. Theoretical Calculations of Interatomic Distances in Certain Crystals.

The generalization of the formula given above for $\phi^{(n)}$, equation (3.04), when the forces between the various ions obey different laws, is easily seen to be

$$\phi^{(n)} = \frac{\lambda_{11} A''_{n_{11}-1}}{(n_{11}-1) r_0^{n_{11}-1}} + \frac{\lambda_{22} A''_{n_{22}-1}}{(n_{22}-1) r_0^{n_{22}-1}} + \frac{2A'_{n_{12}-1} \lambda_{12}}{(n_{12}-1) r_0^{n_{12}-1}}, \quad (5.01)$$

so that the equation to determine r_0 becomes

$$\frac{\lambda_{11} A''_{n_{11}-1}}{r_0^{n_{11}}} + \frac{\lambda_{22} A''_{n_{22}-1}}{r_0^{n_{22}}} + \frac{2\lambda_{12} A'_{n_{12}-1}}{r_0^{n_{12}}} = \frac{(3.495) e^2 z^2}{r_0^2}. \quad (5.02)$$

The last term of the left-hand side is usually the most important and first approximations to r_0 can accordingly be found from

$$r_0^{n_{12}-2} = \frac{2\lambda_{12} A'_{n_{12}-1}}{(3.495) e^2 z^2}.$$

More accurate values of r_0 then follow by successive approximations.

The calculated values of r_0 for certain crystals of the rock-salt type are given in Table XI, the observed values being given in brackets.

As an indication of the relative importance of the terms in the potential $\phi^{(n)}$, we may add that in the case of NaCl it was found that ϕ_{NaNa} (the potential of one Na ion due to all the other Na ions) was $2.178.10^{-14}$, while ϕ_{ClCl} was $5.723.10^{-12}$ and $2\phi_{\text{NaCl}}$ $1.505.10^{-11}$. The relative importance of the terms in equation (5.02) is easily inferred.

It is possible in the same way to calculate the constant of fluorspar. Knowing the force between the metal ions and that between the halogen ions, we need

Table XI.—Calculated and Observed Interatomic Distances in Certain Salts.*

$r_0 10^8$.	Na.	K.	$r_0 10^8$.	Mg.	Ca.
F	2.30 (2.31)	2.63 (2.66)	O	2.10 (2.09)	2.33 (2.40)
Cl	2.85 (2.81)	3.13 (3.14)	S	2.60 (2.54)	2.77 (2.77)

only the force between metal and halogen, and this is readily found by the methods already described. We find, putting $n = 10$,

$$\begin{aligned}\lambda_{\text{CaF}} &= 9.40 \cdot 10^{-81} \\ &= 0.940 \quad (\text{in special units}).\end{aligned}$$

The structure of CaF_2 is well known and need not be described here.† If the length of the unit cube be denoted by $2r_0$, we have, with an obvious notation,

$$\begin{aligned}\phi_{\text{CaCa}} &= \frac{\lambda_{\text{CaCa}} C_{n_{11}-1}}{(n_{11}-1) 2^{(n_{11}-1)/2} r_0^{n_{11}-1}}, & \phi_{\text{FF}} &= \frac{\lambda_{\text{FF}} A_{n_{22}-1}}{(n_{22}-1) r_0^{n_{22}-1}}, \\ \phi_{\text{CaF}} &= \frac{\lambda_{\text{CaF}} D_{n_{12}-1}}{(n_{12}-1) r_0^{n_{12}-1}},\end{aligned}\tag{5.04}$$

where A_s and C_s are triple summations over the lattice points of a simple and face-centred cubic respectively, described and computed in a recent paper,‡ and D_s is given by

$$\begin{aligned}D_s &= 2^s \sum_{\substack{(l_1, l_2, l_3) \\ \text{odd}}} (l_1^2 + l_2^2 + l_3^2)^{-s/2} \\ &= \left(\frac{2}{\sqrt{3}}\right)^s B_s - A_s,\end{aligned}\tag{5.05}$$

B_s being a summation over the lattice points of a body-centred cubic.‡

The total potential energy of a cell is given by

$$\phi = \phi_{\text{CaCa}} + 2\phi_{\text{FF}} + 2\phi_{\text{CaF}} + \phi^{(e)},\tag{5.06}$$

* W. H. Bragg and W. L. Bragg, *loc. cit.*, pp. 166, 300 and 306. Henglein, in a recent paper ('Zs. f. Phys. Chem.', vol. 115, p. 91, 1925) has estimated the crystal constants at absolute zero. He obtains 2.793 for NaCl and 3.116 for KCl. This gives an idea of the correction to be applied to the usual values to obtain corresponding values at absolute zero.

† W. H. Bragg and W. L. Bragg, *loc. cit.*, p. 102; Born, *loc. cit.*, p. 566.

‡ Paper V.

the last term denoting the electrostatic energy per molecule. This has been calculated by Emersleben,* who finds

$$\phi^{(e)} = -\frac{e^2 (5 \cdot 81828)}{a}, \quad (5.07)$$

where a is the smallest *co-ordinate* difference between particles, in this case $r_0/2$.

The condition for equilibrium leads to the following equation in r_0 ,

$$\frac{\lambda_{\text{CaCa}} C_{n_{11}-1}}{2^{(n_{11}-1)/2} r_0^{n_{11}}} + \frac{2\lambda_{\text{FF}} A_{n_{12}-1}}{r_0^{n_{22}}} + \frac{2\lambda_{\text{CaF}} D_{n_{12}-1}}{r_0^{n_{12}}} = \frac{2e^2 (5 \cdot 818)}{r_0^2}. \quad (5.08)$$

Writing $r_0 = \rho \cdot 10^{-8}$ and substituting numerical values, we have

$$a_{(e)} \rho^9 - a_{\text{CaCa}} \rho^2 - a_{\text{CaF}} \rho - a_{\text{FF}} = 0,$$

where

$$a_{(e)} = 2 \cdot 652, \quad a_{\text{CaCa}} = 0 \cdot 1962, \quad a_{\text{CaF}} = 5543, \quad a_{\text{FF}} = 4908.$$

It is to be noted that the repulsive forces between Ca ions have a negligible influence on the crystal constant.

The equation can be solved by Newton's method of successive approximation, leading to the results given in Table XII, in quite good agreement with the observed values.

The crystal constant of CaCl_2 can be calculated in the same way. The result is in the nature of a prediction, for it has not yet been observed.

Table XII.—The Calculated and Observed Constant of Fluorspar.†

	Calculated.			Observed.
	1st Approx.	2nd Approx.	3rd Approx.	
CaF_2	2·798	2·711	2·700	2·745
CaCl_2	3·344	3·344	3·344	—

§ 6. The Compressibilities of Crystals.

Up to now it is the compressibilities of crystals which alone have provided information about the nature of the repulsive fields of ions. The method is

* Emersleben, *loc. cit.*

† Bragg and Bragg, *loc. cit.*, p. 168. Other observations range from 2·70 to 2·745, *cf.* 'Ch. Maguin, La Structure des Cristaux,' p. 231 (1924).

due to Born and Landé,* who, assuming fields of the type considered in this paper, showed how the index could be determined from compressibilities. This work, however, disregarded the dissimilarity between the ions of a crystal and postulated the existence of only one value of n for each crystal. They thus found values of n ranging from about 9 to 11 for various crystals.*

The experimental work which was used to yield these results was that of Richards and Jones,† carried out in 1909, that of Madelung and Fuchs‡ being used in the case of KCl.

By definition, the compressibility is given by

$$\kappa = \frac{1}{V} \frac{dV}{dp}, \quad (6.01)$$

—the specific change of volume by change of pressure. In terms of the potential energy of a crystal, it is easily shown to be given by§

$$\frac{1}{\kappa} = \frac{1}{9\delta} \frac{d^2(\frac{1}{2}\phi_0)}{d\delta^2} \quad (6.02)$$

where $\frac{1}{2}\phi_0$ is the potential energy per cell and δ^3 the volume of a cell.||

In the rock-salt type of crystal, δ is connected with r_0 , the closest distance between atoms, by||

$$\delta = 2^{1/3} r_0, \quad (6.021)$$

so that in this case

$$\frac{1}{\kappa} = \frac{1}{36r_0} \frac{d^2\phi_0}{dr_0^2}. \quad (6.03)$$

Using the equations (3.03), (3.05), (5.01) and (5.02), we find

$$\frac{1}{\kappa} = \frac{1}{36} \left\{ \frac{(n_{11} - n_{12}) \lambda_{n_{11}} A''_{n_{11}-1}}{r_0^{n_{11}+2}} + \frac{(n_{22} - n_{12}) \lambda_{n_{22}} A''_{n_{22}-1}}{r_0^{n_{22}+2}} + \frac{(n_{12} - 2) (3.495) e^2 z^2}{r_0^4} \right\}. \quad (6.04)$$

The calculated and not the observed values of r_0 were used in equation (6.04), as this equation involves the theoretical relation to find r_0 ($\partial\phi/\partial r_0 = 0$). The results given in Table XIII may therefore be regarded as the direct consequence of the values of the force constants previously given.

* Born and Landé, 'Verh. d. Deutsch. Phys. Ges.' vol. 20, p. 210 (1918); Born and Brody, 'Zs. f. Phys.', vol. 11, p. 327 (1922); Born, 'Atomtheorie des festen Zustandes,' 2nd edn., 734 (1923).

† Richards and Jones, 'Journ. Amer. Chem. Soc.', vol. 31, p. 158 (1909).

‡ Madelung u. Fuchs, 'Ann. d. Phys.,' Series 4, vol. 65, p. 289 (1921); Born u. Brody, 'Zs. f. Phys.', vol. 11, p. 327 (1922).

§ Born, *loc. cit.*, p. 569, equation (90").

|| Born, *loc. cit.*, p. 566.

Table XIII.—The Calculated Compressibilities of Crystals.
(Pressures in dynes).

$\kappa \cdot 10^{12}$.	Na.	K.	$\kappa \cdot 10^{12}$	Mg.	Ca.
F	1.40	2.73	O	0.25	0.41
Cl	3.88	6.23	S	0.69	0.96

For only two of these salts, NaCl and KCl, have the compressibilities been measured. The values given are

$$\begin{aligned} \text{NaCl} \quad \kappa_{\text{obs}} &= \left\{ \begin{array}{l} 3.3 \cdot 10^{-12} (*) \\ 4.20 (\dagger) \\ 4.30 (\ddagger) \end{array} \right\} \kappa_{\text{calc.}} = 3.88 \cdot 10^{-12} \\ \text{KCl} \quad \kappa_{\text{obs.}} &= \left\{ \begin{array}{l} 4.8 \cdot 10^{-12} (*) \\ 5.63 (\dagger) \\ 5.2 (\ddagger) \\ 5.62 (\S) \end{array} \right\} \kappa_{\text{calc.}} = 6.23 \cdot 10^{-12} \end{aligned}$$

The agreement can be regarded as satisfactory in view of the fact that the formula for κ involves the force constants directly, and involves as well large powers of the interatomic distance. || Furthermore, integral values of n are used everywhere, and to a first approximation $\kappa (n_{12} - 2)$ is constant, ¶

* J. C. Slater, 'Phys. Rev.,' Ser. II., vol. 23, p. 488, 1924, estimated value at absolute zero, assuming κ to be a linear function of T —a very doubtful assumption. The variation of κ with temperature can be deduced from that of α , the thermal expansion, recently measured by Henglein ('Zs. f. Phys. Chem.,' vol. 115, p. 91 (1925)), by using the theoretical relation $\alpha/\kappa \cdot T^3 = \text{const.}$ (Born, 'Atomtheorie des festen Zustandes,' p. 691, eqn. (359).)

† *Ibid.*, measured at room temperature.

‡ Richards and Saerens, 'Journ. Amer. Chem. Soc.,' vol. 46, p. 934 (1924).

§ Madelung u. Fuchs, 'Ann. d. Phys.,' 4, vol. 65, p. 289 (1921); cf. Born and Brody, 'Zs. f. Phys.,' vol. 11, p. 327, 1922.

|| The limits of error in the determination of the force constants have been indicated in previous papers: Paper 2, pp. 472 and 475; Paper 4, p. 163. They may be taken as (at most) about ± 3 per cent. The numbers of Wasastjerna given in Table I above are used to a high power (8–10), and may involve further errors. The total error in the force constants may be as much as ± 10 per cent. These suffice to give interatomic distances correct to ± 1 per cent.

¶ In a crystal like KCl, where $n_{11} = n_{22} = n_{12}$, the first two terms in equation (6.04) vanish, of course, but even when this is not the case, these terms are very small compared with the last; for instance, in NaCl the numerical values of the terms in the bracket prove to be $1.101 \cdot 10^9$, $-3.562 \cdot 10^{11}$ and $9.634 \cdot 10^{12}$.

so that, if n_{12} is of the order of 10, a change in its value by one integer alters κ by about 10 per cent.

In the same way the compressibility of CaF_2 can be calculated. In this case

$$\frac{1}{\kappa} = \frac{1}{18r_0} \frac{d^2\phi}{dr_0^2},$$

and from equations (5.04), (5.06), (5.07) and (5.08) we have

$$\frac{1}{\kappa} = \frac{1}{18} \left\{ \frac{(n_{11} - n_{12}) \lambda_{\text{FF}} A_{n_{11}-1}}{r_0^{n_{11}+2}} + \frac{(n_{22} - n_{12}) \lambda_{\text{CaCa}} C_{n_{22}-1}}{2^{(n_{22}+1)/2} r_0^{n_{22}+2}} + \frac{(n_{12} - 2) e^2 (5.818)}{r_0^4} \right\}.$$

We thus find (using the calculated value of $r_0 = 2.695$) the value $0.87.10^{-12}$ for κ . The observed value is* $1.16.10^{-12}$.

§ 7. The Elastic Constants.

The first theoretical calculations of elastic constants were made by Born,[†] who made the assumption (in the notation of this paper) that $n_{11} = n_{22} = n_{12} = 10$, and $\lambda_{11} = \lambda_{22} = \lambda_{12}$. This simplifies the formulæ considerably, for it is then possible to calculate the value of the elastic constant without a knowledge of the repulsive force constant, for it can be eliminated by the relation $\partial\phi/\partial r = 0$. In a later paper by Born and Brody[‡] formulæ were obtained in a rather more general form. The values of n_{11} , n_{22} and n_{12} were still assumed to be the same, but the force constants were taken to be different. The latter appeared in the formulæ in the form of a ratio $(\lambda_{11} + \lambda_{22})/2\lambda_{12}$ ($= \beta$), which was regarded as a variable parameter and adjusted to give agreement between theory and observation. The value required in the two cases for which there were experimental results, viz., NaCl and KCl, proved to be the same but was *negative* in sign, viz., $\beta = -0.5$. Such a value indicates that while neighbouring atoms *repel*, alternate atoms *attract*—a somewhat paradoxical result, hardly likely to find acceptance until some physical interpretation of its nature is forthcoming.

Born§ has obtained general formulæ for the elastic constants, as of other properties of a crystal, in terms of the forces between the various constituent

* Born, *loc. cit.*, p. 747.

† Born, 'Ann. d. Phys.,' vol. 61, p. 87 (1919).

‡ Born and Brody, 'Zs. f. Phys.,' vol. 11, p. 327 (1922).

§ Born, 'Atomtheorie des festen Zustandes,' 2nd edn. (1923), §§ 6, 8 and 13.

particles. A formula for each of the 21 elastic constants, defined in the usual way as the coefficients of the linear relation between stress and strain,

$$-\mathbf{X}_x = c_{11}x_x + c_{12}y_y + c_{13}z_z + c_{14}y_z + c_{15}z_x + c_{16}x_y \quad (7.01)$$

is given, involving certain triple summations over the lattice points of the crystal.

The number of independent elastic constants in a crystal of the rock-salt type reduce to two. For instance, the compressibility is given in terms of c_{11} and c_{12} by*

$$\frac{1}{\kappa} = \frac{1}{3}(c_{11} + 2c_{12}). \quad (7.02)$$

Hence having already calculated κ above, we need now only calculate one other elastic constant, say c_{11} . For this we have in Born's notation†

$$c_{11} = \frac{1}{2\Delta} \sum_{kk'} \sum_l \left[\frac{1}{r} \frac{d}{dr} \left(\frac{1}{r} \frac{d\phi_{kk'}}{dr} \right) \right]_l (x_{kk'}^l)^4 \quad (k, k' = 1, 2) \quad (7.03)$$

where $\phi_{kk'}$ is the potential between a k atom and a k' atom, their distance apart being denoted by $r_{kk'}^l$, and Δ is the volume of unit cell.

If the charge on the particles k and k' be denoted respectively by $z_k e$ and $z_{k'} e$, we have in the notation of this paper

$$\phi_{kk'} = -\frac{z_k z_{k'} e^2}{r} - \frac{\lambda_{kk'}}{(n_{kk'} - 1) r^{n_{kk'} - 1}}, \quad (7.04)$$

and so we find

$$c_{11} = \frac{1}{2\Delta} \sum_{kk'} \sum_l \left[\frac{3z_k z_{k'} e^2}{(r_{kk'}^l)^5} + \frac{(n_{kk'} + 1) \lambda_{kk'}}{(r_{kk'}^l)^{n_{kk'} + 3}} \right] (x_{kk'}^l)^4. \quad (7.05)$$

For a crystal like NaCl, this can be shown to lead to

$$c_{11} = -\alpha + \beta_{11} + \beta_{22} + 2\beta_{12} \quad (7.06)$$

where

$$\alpha = \frac{e^2}{2r_0^4} \{S_1'(1) - S_1''(1)\}, \quad (7.07)$$

$$\beta_{kk} = \frac{(n_{kk} + 1) \lambda_{kk}}{12r_0^{n_{kk} + 2}} S_1''(n_{kk} - 1) \quad (k = 1, 2), \quad (7.08)$$

$$\beta_{12} = \frac{(n_{12} + 1) \lambda_{12}}{12r_0^{n_{12} + 2}} S_1'(n_{12} - 1), \quad (7.09)$$

* Born, *loc. cit.*, equation (90).

† Born, *loc. cit.*, equations (88), (84) and (16).

the notation being that of Born, viz.,

$$\begin{aligned}
 S_1'(p) &= 3 \sum_{\substack{(l_1+l_2+l_3) \\ \text{odd}}} (l_1^2+l_2^2+l_3^2)^{-\frac{p+4}{2}} l_1^4 \\
 &= 3 \sum_l \{ (1+l_2+l_3)^2 + (1+l_3+l_1)^2 + (1+l_1+l_2)^2 \}^{-\frac{p+4}{2}} (1+l_2+l_3)^4, \\
 S_1''(p) &= 3 \sum_{\substack{(l_1+l_2+l_3) \\ \text{even}}} (l_1^2+l_2^2+l_3^2)^{-\frac{p+4}{2}} l_1^4 \\
 &= 3 \sum_l \{ (l_2+l_3)^2 + (l_3+l_1)^2 + (l_1+l_2)^2 \}^{-\frac{p+4}{2}} (l_2+l_3)^4.
 \end{aligned}$$

The numerical values of some of these coefficients have been calculated by Born*; thus, he finds,

$$S_1(1) = S_1'(1) - S_1''(1) = 3 \cdot 226.$$

He also has given the values of $S_1'(p)$ and $S_1''(p)$ calculated by direct summation† for $p = 7, 8, 9$ and 10 . These are used in calculating the results given in Table XIV. As in the case of compressibility, the latter are a direct consequence of the force constants given in this paper.

Table XIV. Calculated Values of Young's Modulus.

	NaF.	NaCl.	KF.	KCl.	MgO.	MgS.	CaO.	CaS.
$\alpha \cdot 10^{-11}$	13.17	5.57	7.67	3.818	75.56	32.08	50.34	24.81
$\beta_{11} \cdot 10^{-11}$	0.09	0.005	0.38	0.056	0.07	0.004	0.75	0.11
$\beta_{22} \cdot 10^{-11}$	1.46	1.46	0.25	0.516	21.76	12.20	5.81	6.02
$2\beta_{12} \cdot 10^{-11}$	25.22	7.70	13.75	5.614	118.6	35.99	86.48	31.70
$c_{11} \cdot 10^{-11}$	13.60	3.60	6.71	2.368	64.8	16.11	42.70	13.02

(β_{11} refers to the contribution of the metal ions alone.)

The only two observations with which they can be compared are those of NaCl and KCl by Voigt,‡ who finds

$$\begin{array}{llllll}
 \text{NaCl} & .. & .. & .. & .. & c_{11} = 4.68.10^{11} \\
 \text{KCl} & .. & .. & .. & .. & c_{11} = 3.68.10^{11}.
 \end{array}$$

The agreement between observation and theory is only fair. The discrepancy may partly be accounted for by the limited accuracy of the force constants and partly by inaccuracies in the length r_0 . A 1 per cent. error in the latter involves a 10 per cent. error in β_{12} (the largest term in c_{11}), and, as c_{11}

* Born, *loc. cit.*, p. 738, equation (453").

† Born, *loc. cit.*, p. 739, Table XI.

‡ Voigt, *Lehrbuch der Kristallphysik*, § 373, p. 744; Born, *loc. cit.*, p. 739.

depends on the difference of β_{12} and α , such an error in β_{12} may involve an error of about 20 per cent. in c_{11} . Furthermore a change in n by one integer changes β_{12} by 10 per cent., and so for a like reason may change c_{11} by 20 per cent.

The formula for c_{11} is, therefore, seen to be very sensitive to changes of λ , n and r_0 , and great accuracy cannot be expected. The reverse process of finding information about the forces from observations of the elastic constants seems more promising, if these could be obtained with sufficient accuracy for the crystals considered here.

§ 8. The Surface Energy.

If Φ_{12} denote the mutual potential energy of the parts of a crystal separated by a plane, then the surface energy per unit area of the dividing plane can be shown to be

$$\sigma = -\frac{\Phi_{12}}{2F} \quad (8.01)$$

approximately, where F is the area of the plane. In this formula the shrinking of the boundary of each part in any actual division of the crystal is neglected, but this can be shown to be of a lower order of magnitude than the expression here given.* If the elementary cell of the crystal be arranged so that two of its vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$, lie in the plane, then it follows that

$$\sigma = -\frac{1}{2|a_1a_2|} \sum_{kk'} \sum_{l_3 \geq 0} \sum_{p=1}^{\infty} \phi_{kk'}^{l_1, l_2, l_3+p}, \quad (8.02)$$

an expression giving the potential energy of the one part of the crystal on that column of the other part having the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ as its base, and $\mathbf{a}_3$ as its direction. The term $\phi_{kk'}^{l_1, l_2, l_3+p}$ denotes the potential of the k th particle of the cell l_1, l_2, l_3 (*i.e.*, whose base point is $l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3$ on the k' particle of the p^{th} cell of the column). As this term appears (l_3+p) times in the summation, the expression for σ simplifies to

$$\sigma = -\frac{1}{2|a_1a_2|} \sum_{kk'} \sum_{l_3 > 0} l_3 \phi_{kk'}^{l_1, l_2}. \quad (8.03)$$

For instance, in the case of NaCl, for a plane perpendicular to one of the cubic axes, say, a (1, 0, 0) plane, we have

$$\mathbf{a}_1 = r_0 (\mathbf{i}_1 + \mathbf{i}_2), \quad \mathbf{a}_2 = r_0 (-\mathbf{i}_1 + \mathbf{i}_2) \quad (8.04)$$

where r_0 is the distance between a Na ion and the nearest Cl ion and $\mathbf{i}_1$ and $\mathbf{i}_2$ are unit vectors parallel to the crystal axes, so that $|\mathbf{a}_1 \mathbf{a}_2| = 2 r_0^2$. The

* Cf. Born, *loc. cit.*, p. 538, *et seq.*

potential ϕ_{kl} being given by (7.04), the expression for σ in this case becomes

$$\sigma_{100} = -\frac{1}{4r_0^2} \left\{ \frac{2e^2}{r_0} s_0(1) + \frac{\lambda_{11} s_0''(n_{11}-1)}{(n_{11}-1) r_0^{n_{11}-1}} + \frac{\lambda_{22} s_0''(n_{22}-1)}{(n_{22}-1) r_0^{n_{22}-1}} + \frac{2\lambda_{12} s_0'(n_{12}-1)}{(n_{12}-1) r_0^{n_{12}-1}} \right\}, \quad (8.05)$$

where

$$s_0(1) = \sum_{l_1 \geq 1} \frac{l_1 (-1)^{l_1+l_2+l_3}}{(l_1^2 + l_2^2 + l_3^2)^{\frac{5}{2}}} \quad (8.06)$$

$$s_0'(n) = \sum_{\substack{l_1 > 0 \\ (l_1+l_2+l_3) \text{ odd}}} \frac{l_1}{(l_1^2 + l_2^2 + l_3^2)^{n/2}} \quad (8.07)$$

and

$$s_0''(n) = \sum_{\substack{l_1 > 0 \\ (l_1+l_2+l_3) \text{ even}}} \frac{l_1}{(l_1^2 + l_2^2 + l_3^2)^{n/2}}. \quad (8.08)$$

For the numerical applications of the formulæ, values of $s_0'(n)$ and $s_0''(n)$ have been calculated by direct summation for values of n equal to 8, 9 and 10. The number of terms taken extended as far as $l_1^2 + l_2^2 + l_3^2 = 30$, so that the summation should be accurate as far as the third decimal place at least. The results are given in the following table:—

Table XV.—The Value of certain triple Summations.

n .	s_0' .	s_0'' .
8	1.075	0.2763
9	1.039	0.187*
10	1.021	0.1295

* Obtained by using s_0'' and the value of $s_0(n) = s_0'(n) + s_0''(n)$ given by Born, p. 743. This value is not used here.

The value of $s_0(1)$ is given by Born* as being -0.0650 . The values of σ_{100} , which follow from the force constants already given in this paper, are given for eight salts in Table XVI.

Table XVI.—The Surface Energies of certain Salts (1, 0, 0 plane).

σ_{100} .	F.	Cl.	σ_{100} .	O.	S.
Na	304	96	Mg	1,362	357
K	180	76.6	Ca	1,032	356

* Born, *loc. cit.*, p. 743.

The only experimental evidence for values of σ is that of σ for the molten state. The observed values are*

$$\text{NaCl} \quad \sigma = 66.5 \text{ ergs,}$$

$$\text{KCl} \quad \sigma = 69.3 \text{ ergs,}$$

which are of the right order of magnitude but less than the calculated, as is to be expected for the high temperatures to which they apply. The values of σ_{100} calculated by Born† on the assumption of a general value of $n = 10$ for the repulsive index are

$$\text{NaCl} \quad \sigma = 150.2, \quad \text{KCl} \quad \sigma = 107.5 \quad (\text{Born}).$$

In the same way the surface energy for other planes in the crystals can be calculated. For instance, in the case of the (0, 1, 1) plane, we can choose the unit cell of the crystal so that one of its faces, lying in the plane, is a rectangle of sides $2r_0$ and $r_0\sqrt{2}$ formed by 4 Na atoms. If these edges are used as rectangular axes and a third axis is taken perpendicular to the plane, the vectors of the crystal become

$$\mathbf{a}_1 = (2r_0, 0, 0), \quad \mathbf{a}_2 = (0, r_0\sqrt{2}, 0) \quad \text{and} \quad \mathbf{a}_3 = \left(r_0, \frac{r_0}{\sqrt{2}}, \frac{r_0}{\sqrt{2}}\right).$$

The expression for σ_{011} becomes

$$\sigma_{011} = -\frac{e^2}{2\sqrt{2}r_0^3} s_1(1) - \frac{\lambda_{11}s_1''(n_{11}-1)}{4\sqrt{2}(n_{11}-1)r_0^{n_{11}+1}} - \frac{\lambda_{22}s_1''(n_{22}-1)}{4\sqrt{2}(n_{22}-1)r_0^{n_{22}+1}} - \frac{\lambda_{12}s_1'(n_{12}-1)}{2\sqrt{2}(n_{12}-1)r_0^{n_{12}+1}} \quad (8.09)$$

where

$$\begin{aligned} s_1(1) &= \sum_{l_3 > 0} \left\{ \frac{(-1)^{l_3} l_3}{\{(l_1 + l_3)^2 + 2l_2^2 + 2l_2l_3 + l_3^2\}^{\frac{1}{2}}} \right\} \\ &= \sum_{(m_2+m_3) > 0} \frac{(-1)^{m_1-m_2-m_3} (m_2 + m_3)}{(m_1^2 + m_2^2 + m_3^2)^{\frac{1}{2}}} \\ &= \sum_{(m_2+m_3) > 0} \frac{2S}{(m_1^2 + m_2^2 + m_3^2)^{\frac{1}{2}}} \frac{(-1)^{m_1-m_2-m_3} m_3}{(m_1^2 + m_2^2 + m_3^2)^{\frac{1}{2}}} \end{aligned} \quad (8.10)$$

and

$$s_1'(n) = \sum_{\substack{(m_2+m_3) > 0 \\ (m_1+m_2+m_3) \text{ odd}}} \frac{2S}{(m_1^2 + m_2^2 + m_3^2)^{n/2}} \frac{m_3}{(m_1^2 + m_2^2 + m_3^2)^{n/2}} \quad (8.11)$$

$$s_1''(n) = \sum_{\substack{(m_2+m_3) > 0 \\ (m_1+m_2+m_3) \text{ even}}} \frac{2S}{(m_1^2 + m_2^2 + m_3^2)^{n/2}} \frac{m_3}{(m_1^2 + m_2^2 + m_3^2)^{n/2}} \quad (8.12)$$

* Born, *loc. cit.*, p. 743.

† Born, p. 743; Born and Sterne, 'Berl. Ber.', p. 901 (1919).

Some numerical values of these functions are given below, obtained by direct summation :—

Table XVII.—The Values of Certain Triple Summations.

$n.$	$s_1'(n).$	$s_1''(n).$
8	2.091	0.4094
9	2.046	0.279*
10	2.024	0.1938

* Obtained from $s_1'(n)$ and $s_1'(n) + s_1''(n)$ given by Born and Sterne, 'Berl. Ber.' p. 910. This value is not required here.

The value of $s_1(1)$ is given by Born and Sterne* in the form $s_1(1)/2\sqrt{2} = 0.06347$, so that $\frac{e^2 s_1(1)}{2\sqrt{2}} = 1.446.10^{-20}$. The values of σ_{011} prove to be as follows :—

Table XVIII.—Surface Energies of Certain Salts (0, 1, 1 plane).

σ_{011} .	F.	Cl.	σ_{011} .	O.	S.
Na	784	350	Mg	3940	1730
K	489	260	Ca	2850	1440

What is more interesting than the actual value of σ_{011} is its ratio to σ_{100} . These are given in Table XIX, whence it is evident that in all cases $\sigma_{011}/\sigma_{100} > \sqrt{2}$, showing that the net plane (0, 1, 1) does not form a natural face of the crystal. This is in accord with observation. Born and Sterne obtain the value 2.71 for $\sigma_{011}/\sigma_{100}$ in all cases.

Table XIX.—The Calculated Ratio of the Surface Energies for the (0, 1, 1) Plane and the (1, 0, 0) Plane.

$\sigma_{011}/\sigma_{100}$.	F.	Cl.	$\sigma_{011}/\sigma_{100}$.	O.	S.
Na	2.58	3.76	Mg	2.89	4.84
K	2.72	3.39	Ca	2.76	4.02

* *Loc. cit.*

§ 9. The Edge Energy.

Suppose that a very large crystal be divided by two intersecting planes into parts 1, 2, 3 and 4. Let F_1 and F_2 be the areas of the planes. The work required to separate the crystal into the two parts divided by F_1 is

$$-(\Phi_{13} + \Phi_{14} + \Phi_{23} + \Phi_{24}).$$

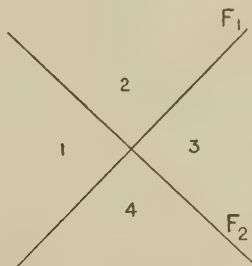


FIG. 2. (F_1 and F_2 not necessarily at right angles.)

If, however, the crystal had previously been divided across F_2 , the work required to complete the division across F_1 would only be

$$-(\Phi_{14} + \Phi_{23}). \quad (9.02)$$

The difference between this and the former expression is defined as the *edge energy*. If this be measured in terms of unit-length of the four edges resulting from the crystal division, and denoted by k , we then have

$$k = \frac{\Phi_{13} + \Phi_{24}}{4L}. \quad (9.03)$$

By an argument analogous to that used in the last paragraph it can then be shown that*

$$k = \frac{1}{4|a_3|} \sum_{kk'} \sum_{(l_1, l_2) \geq 0} l_1 l_2 \phi_{kk'}^l, \quad (9.04)$$

where a_3 is the vector of the crystal cell in the direction of the edge. If, for instance, in the case of NaCl the edge considered be one of the cubic axes, then

$$a_3 = 2r_0 \mathbf{i}_3 \quad (9.05)$$

where r_0 is the nearest distance between two Na atoms and $\mathbf{i}_1$, $\mathbf{i}_2$ and $\mathbf{i}_3$ are unit vectors along the cubic axes, $0x$, $0y$ and $0z$; corresponding to a_3 the other vectors of the unit cell are

$$a_1 = r_0 (\mathbf{i}_1 + \mathbf{i}_3) \quad (9.06)$$

and

$$a_2 = r_0 (\mathbf{i}_2 + \mathbf{i}_3). \quad (9.07)$$

* Born, *loc. cit.*, p. 543.

The calculations are simplified by virtue of the fact that the vectors $\mathbf{a}_1$ and $\mathbf{a}_3$ lie in the plane xz , while $\mathbf{a}_2$ and $\mathbf{a}_3$ lie in yz , so that corresponding to the divisions 1, 2, 3 and 4 in the figure above we have the quadrants bounded by the axes Ox and Oy . It is then clear from symmetry that $\Phi_{13} = \Phi_{24}$. It therefore follows that

$$k = \frac{\Phi_{13}}{4r_0}, \quad (9.08)$$

since $L = 2r_0$, and hence that

$$k = \frac{1}{4r_0} \left\{ \frac{2e^2 z^2 s_2(1)}{r_0} + \frac{\lambda_{11} s_2''(n_{11} - 1)}{(n_{11} - 1) r_0^{n_{11}-1}} + \frac{\lambda_{22} s_2''(n_{22} - 1)}{(n_{22} - 1) r_0^{n_{22}-1}} + \frac{2\lambda_{12} s_2'(n_{12} - 1)}{(n_{12} - 1) r_0^{n_{12}-1}} \right\} \quad (9.09)$$

where

$$s_2(1) = \sum_{l_1, l_2 \geq 0} \frac{(-1)^{l_1+l_2+l_3} l_1 l_2}{(l_1^2 + l_2^2 + l_3^2)^{\frac{3}{2}}} \quad (9.10)$$

and

$$s_2'(n) = \sum_{\substack{l_1, l_2 \geq 0 \\ (l_1+l_2+l_3) \text{ odd}}} \frac{l_1 l_2}{(l_1^2 + l_2^2 + l_3^2)^{n/2}} \quad (9.11)$$

$$s_2''(n) = \sum_{\substack{l_1, l_2 \geq 0 \\ (l_1+l_2+l_3) \text{ even}}} \frac{l_1 l_2}{(l_1^2 + l_2^2 + l_3^2)^{n/2}}. \quad (9.12)$$

The same result can be obtained more formally by considering the distances between atoms in terms of the vectors of the cell which we have chosen above. With an obvious notation we have

$$\mathbf{r}_{11}^i = \mathbf{r}_{22}^i = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3, \quad (9.13)$$

$$\mathbf{r}_{12}^i = -\mathbf{r}_{21}^i = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3. \quad (9.14)$$

So that

$$|\mathbf{r}_{11}^i| = |\mathbf{r}_{22}^i| = r_0 \{l_1^2 + l_2^2 + (l_1 + l_2 + 2l_3)^2\}^{\frac{1}{2}}, \quad (9.15)$$

$$|\mathbf{r}_{12}^i| = |\mathbf{r}_{21}^i| = r_0 \{l_1^2 + l_2^2 + (l_1 + l_2 + 2l_3 + 1)^2\}^{\frac{1}{2}}. \quad (9.16)$$

The expression for k given above (equation (9.09)) then follows, provided

$$s_2(1) = \sum_{l_1, l_2 \geq 0} \left[\frac{l_1 l_2}{\{l_1^2 + l_2^2 + (l_1 + l_2 + 2l_3)^2\}^{\frac{3}{2}}} - \frac{l_1 l_2}{\{l_1^2 + l_2^2 + (l_1 + l_2 + 2l_3 + 1)^2\}^{\frac{3}{2}}} \right]$$

and

$$s_2'(n) = \sum_{l_1, l_2 \geq 0} \frac{l_1 l_2}{\{l_1^2 + l_2^2 + (l_1 + l_2 + 2l_3 + 1)^2\}^{n/2}}$$

$$s_2''(n) = \sum_{l_1, l_2 \geq 0} \frac{l_1 l_2}{\{l_1^2 + l_2^2 + (l_1 + l_2 + 2l_3)^2\}^{n/2}}.$$

These can obviously be transformed to the simple forms already given.

The value of $s_2(1)$ is given by Born and Sterne* as 0.021865, while the values of $s_2'(n)$ and $s_2''(n)$ for $n = 8, 9$ and 10 are as given in Table XX.

Table XX.—The Values of Certain Triple Summations.

$n.$	$s_2'(n).$	$s_2''(n).$
8	0.0365	0.0745
9	0.0187	0.0484*
10	0.00997	0.03288

* From $s_2'(9) + s_2''(9) = 0.06704$, given by Born and Sterne, *loc. cit.* This value is not used in the subsequent work.

For the sake of completeness the values of k for the cubic crystals considered in this paper have been calculated and are given in the following table, although there is no experimental evidence with which to compare them.

Table XXI.—Calculated Values of the Edge Energy of Certain Salts.

$k \cdot 10^{-6}.$	F.	Cl.	$k \cdot 10^{-6}.$	O.	S.
Na	5.13	3.97	Mg	27.0	20.8
K	3.95	3.06	Ca	20.5	16.8

Born and Sterne† have also calculated the edge energy, using the simple formula

$$k = 0.0119 \frac{e^2}{r_0^2} = 1.945 \cdot 10^{-5} \left(\frac{\rho}{M_1 + M_2} \right)^{\frac{2}{3}} \text{ ergs. cm.}^{-1},$$

from which we find the following values :—

$$\begin{aligned} \text{NaCl,} \quad k_{\text{calc.}} &= 2.16 \cdot 10^{-6} \\ \text{KCl,} \quad k_{\text{calc.}} &= 1.73 \cdot 10^{-6}. \end{aligned}$$

§ 10. The Energy of a Crystal.

We have already shown above‡ that for a crystal of the rock-salt type the potential energy per unit cell, containing one metal and one halogen ion, is given by

$$\frac{1}{2}\phi = \frac{1}{2} \left\{ \frac{\lambda_{11}A''_{n_{11}-1}}{(n_{11}-1)r_0^{n_{11}-1}} + \frac{\lambda_{22}A''_{n_{22}-1}}{(n_{22}-1)r_0^{n_{22}-1}} + \frac{2\lambda_{12}A'_{n_{12}-1}}{(n_{12}-1)r_0^{n_{12}-1}} - \frac{7.966 \cdot 10^{-19} \cdot z^2}{r_0} \right\} \quad (10.01)$$

* Born and Sterne, *loc. cit.*, p. 913.

† Born and Sterne, *loc. cit.*, ; Born, *loc. cit.*, p. 744.

‡ Equations (5.01), (3.03), (3.05) and (3.07).

while the crystal energy per gram-molecule is

$$U = -\frac{N}{2}\phi,$$

where N is the usual Avogadro or Loschmidt Number ($6.062 \cdot 10^{23}$). Expressed in calories per gram-molecule, we have

$$U = -\frac{N}{2J}\phi,$$

where J is the mechanical equivalent of heat ($4.184 \cdot 10^7$). The calculated values of U are as follows :—

Table XXII.—Calculated Values of Crystal Energies (in kilocalories).

U.	F.	Cl.	U.	O.	S.
Na	226	179	Mg	989	784
K	195	161	Ca	884	728

Born has deduced the value of U for several crystals from experimental data by means of certain simple thermo-chemical relations, conveniently exhibited by him diagrammatically in the form of the “Born” cycle.* The only two of the crystals considered here for which U is thus determined are NaCl and KCl, and the values are reproduced in the following table.

Table XXIII.—Observed and Calculated Values of Crystal Energies.

	“ Observed.”	Calc. (Born).	Calc.
NaCl	183	182	179
KCl	165	162	161

The values calculated by the methods of this paper may be regarded as in satisfactory agreement with the “observed” values, for they are well within the limits of experimental error of the latter, seeing that these depend on certain observations (as, for example, the heat of dissociation of hydrogen) which are not known to a great degree of accuracy.

In the same way the crystal energy of CaF_2 and crystals of the same type may be calculated by means of the formula :—

$$U = \frac{N}{2} \left\{ \frac{5.818e^2}{(r_0/2)} - \frac{\lambda_{11}C_{n_{11}-1}}{(n_{11}-1)2^{(n_{11}-1)/2}r_0^{n_{11}-1}} - \frac{\lambda_{22}A_{n_{22}-1}}{(n_{22}-1)r_0^{n_{22}-1}} - \frac{2\lambda_{12}D_{n_{12}-1}}{(n_{12}-1)r_0^{n_{12}-1}} \right\},$$

* Born, *loc cit.*, p. 748.

λ_{11} and λ_{22} referring, as in equations (5.04) and (5.08) above, to the repulsive forces between Ca and F ions respectively. Using the force constants already given, we find

$$U_{\text{CaF}_2} = 635 \text{ kilocal.}$$

This is to be compared with the value calculated by Born on the assumption of a general repulsive field according to the inverse 10th power, which is given as

$$U_{\text{CaF}_2} = 609 \text{ kilocal. (calculated by Born).}$$

The corresponding results for CaCl_2 are

$$U_{\text{CaCl}_2} = \begin{cases} 503 \text{ kilocal.} \\ 480 \text{ kilocal. (Born).} \end{cases}$$

§ 11. *The Properties of Crystalline Argon.*

Solid argon has been shown recently* to be a crystal of the face-centred cubic type, with a crystal constant of $3.84 \text{ \AA}$, a fact satisfactorily explained in a former paper† on the basis of a repulsive field according to an inverse 15th power and an attractive field according to an inverse 5th. With force constants obtained from a consideration of the equation of state of this gas,‡ a theoretical value of $3.86 \text{ \AA}$ was obtained. There remains now for discussion how this result is affected by the modifications introduced in this Paper.

Formerly we assumed the repulsive fields of C^- , A and K^+ to be the same, and this led us to suppose that their repulsive fields were according to an inverse 15th power. Now that we have taken into account the difference in the size of Cl^- and K^+ and have obtained different force constants for them, we have obtained a repulsive index of 9 instead of 15.

The natural presumption is that argon atoms repel according to an inverse 9th-power law. Corresponding to a repulsion of this type, we found§ an attraction $\lambda_5 r^{-5}$ with $\lambda_5 = 1.625.10^{-43}$. For a law of force $\frac{\lambda_n}{r^n} - \frac{\lambda_m}{r^m}$, the potential of one atom of crystalline argon due to the rest is

$$\phi = \frac{\lambda_n C_{n-1}}{(n-1) r_0^{n-1}} - \frac{\lambda_m C_{m-1}}{(m-1) r_0^{m-1}} \quad (11.02)$$

where r_0 is the closest distance between atoms and C_n is a *crystal potential constant* already defined above.||

* Simon u. Simson, 'Zs. f. Phys.,' vol. 21, p. 168 (1924); vol. 25, p. 160 (1924).

† Paper III.

‡ Paper II.

§ Paper II., p. 477.

|| Paper V.

The value of r_0 is therefore given by

$$r_0 = \left(\frac{\lambda_n C_{n-1}}{\lambda_m C_{m-1}} \right)^{1/(n-m)}, \quad (11.03)$$

and substituting the values appropriate to $n = 9$ and $m = 5$, we obtain $r_0 = 4.21 \text{ \AA}$, a result which is 10 per cent. greater than the observed value.

Again, the heat of sublimation of argon is known, and, as this can be calculated theoretically, it forms another check on the atomic field. The heat of sublimation, Φ , is equal, in appropriate units, to the work required to separate one gram-atom of a crystal into its constituent atoms, and so, in terms of ϕ given above,

$$\Phi = -\frac{N}{2}\phi \text{ ergs.} = -\frac{N}{2J}\phi \text{ calories.}$$

In virtue of (11.03), this can be expressed in the alternative forms

$$\Phi = \frac{(n-m)N}{(n-1)(m-1)2J} \frac{\lambda_n C_{n-1}}{r_0^{n-1}}, \quad (11.05)$$

and

$$\Phi = \frac{(n-m)N}{(n-1)(m-1)2J} \frac{(\lambda_m C_{m-1})^{n-1/n-m}}{(\lambda_n C_{n-1})^{m-1/n-m}}. \quad (11.06)$$

With the values of λ_n and λ_m appropriate to $n = 9$ and $m = 5$, taking C_{m-1} and C_{n-1} from the table of a recent paper,* we find $\Phi = 1190$ calories, whereas the value deduced by F. Born† from measurements of the vapour pressure of pure argon is 1,835 calories. It is evident, therefore, that this atomic model is inadequate to explain the properties of crystalline argon.

In order to investigate whether an improvement would be effected by a change of m , n remaining unaltered, a further application of the methods described in a former paper on the equation of state has been made. In doing so, the new work of Holborn and Otto‡ on the isotherms of argon at low temperatures was taken into account. The new values of the virial coefficient, B , were found in the usual units to be

T	173.1	223.1	273.1
log B	$\bar{3}.458 (n)$	$\bar{3}.227 (n)$	$\bar{4}.994 (n)$

and were found to lie on a curve continuous with the former values (see fig. 3). The values of m considered were $5\frac{1}{2}$ and 6. The theoretical curves for the virial coefficient, when plotted in the way described in the former paper, fitted the

* Paper V.

† F. Born, 'Ann. der Physik,' vol. 69, p. 473 (1922).

‡ Holborn and Otto, 'Zs. f. Phys.,' vol. 30, p. 320 (1924).

experimental points quite closely and, from the fitting of experimental and theoretical curves, the values of the appropriate force constants were deduced. In case the results should be needed for any other purpose they are here quoted,

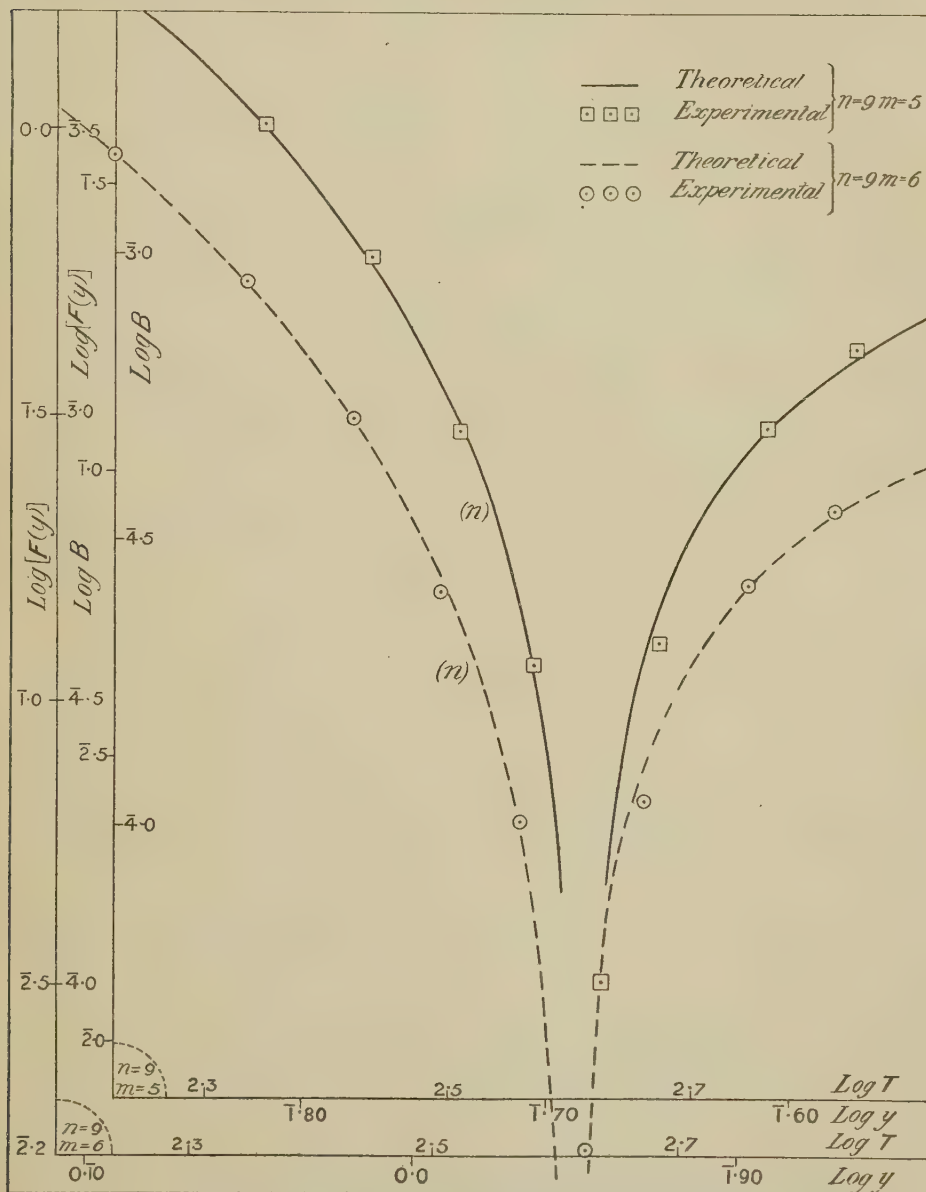


Fig. 3.—The theoretical curves for the second virial coefficient for the models $\lambda_n r^{-n} - \lambda_m r^{-m}$ with $(n=9, m=5\frac{1}{2})$, $(n=9, m=6)$ and the experimental values for argon (cf., figs. 2 and 3, Paper II, *loc. cit.*).

and the figure is given to show the sort of agreement between theory and experiment.

Table XXIV.—The Force Constants of Argon for Various Atomic Models.*

n .	m .	X.	Y.	λ_n .	λ_m .	σ .
9	5	0.990	3.622	$1.009 \cdot 10^{-72}$	$1.6248 \cdot 10^{-43}$	$7.053 \text{ \AA}$
9	$5\frac{1}{2}$	0.9895	3.55	$1.240 \cdot 10^{-72}$	$5.586 \cdot 10^{-47}$	7.238
9	6	0.9311	3.50	$1.518 \cdot 10^{-72}$	$1.700 \cdot 10^{-50}$	7.423

The value of C_{m-1} for $m = 5\frac{1}{2}$ was obtained by expressing C_m as a quartic in m in the form

$$C_m = \alpha + \beta (m - 6) + \gamma (m - 6)^2 + \delta (m - 6)^3 + \varepsilon (m - 6)^4$$

and determining the constants α , β , γ , δ and ε to give the right values for C_4 , C_5 , C_6 , C_7 , and C_8 . The resulting value for $C_{4\frac{1}{2}}$ was found to be 20.00. [A cubic curve through C_4 , C_5 , C_6 and C_7 gave $C_{4\frac{1}{2}} = 20.14$, and a quadratic through C_4 , C_5 and C_6 the value 20.42.]

The values of r_0 and Φ which follow from these results are given in Table XXV.

Table XXV.—Calculated Constants of Crystalline Argon.

m .	r_0 (in $\text{\AA}$).	Φ (in cal.).
5	4.21	1190
$5\frac{1}{2}$	4.12	1350
6	4.07	1410

None of these models suffices to explain the facts. Two further possibilities suggest themselves. In the first place, we may give a still higher value to m (say, $m = 7$) for r_0 (calc.) and Φ (calc.) vary together and in the right direction. This possibility must, however, be dismissed for the following reason: the values of the repulsive constant λ_n increase when m increases, even when n remains fixed (see Table 24, where λ_9 is equal $1.009 \cdot 10^{-72}$ when $m = 5$ and to $1.518 \cdot 10^{-72}$ when $m = 6$). Consequently if, throughout the whole of the investigation, m had been taken equal to 6, all the force constants in Table IV above for Cl^- and K^+ would have been increased, and hence all the values of the calculated distances in the crystal KCl given in Table VI would have been increased. It follows that the value of n required to give agreement between theoretical and observed distances in KCl would no longer be 9, but would be smaller. This

* The notation is that of Paper II.

would then cause large discrepancies between observed and calculated values of the compressibilities.

The present comparatively good agreement between theory and observation in the case of crystal distances, compressibilities and energies (Tables XI, XIII and XXIII) indicates that the value of n is approximately right.

An alternative supposition is that a repulsive force of the type $\lambda_n r^{-n}$ cannot represent actual fields over the whole range of r ; in fact, it would be very surprising if it did. In all probability a function of this type only represents the actual facts over a small range of r , and outside this range the character of the function must be modified.* In other words, a force λr^{-9} may be a sufficiently good representation of the repulsive field of an argon-like core at distances of about 3 Å (as in KCl, CaS), but at greater distances (such as 3.84 Å in crystalline argon) a different law of force is necessary. Support for this may be found in the fact that when n is taken to be 15 (and $m = 5$) the calculated value of r_0 for crystalline argon is 3.86 Å, which is in excellent agreement with the observed value of 3.84 Å, the difference between the calculated and observed values being within the limits of error of the force constants.† Again, if the value 3.84 Å is used for r_0 in the expression (11.05) for Φ , with the value of λ_n for $n = 15$, $m = 5$, we find

$$\Phi = 1,772 \text{ cal.},$$

while the value deduced from the experimental work of F. Born is $1,835 \pm 5$ —as good agreement as can be hoped for with integral values of n and m . The evidence therefore points to the law of force r^{-15} at large distances and the law r^{-9} at small distances.

A function of r , which approximates to $\lambda_9 r^{-9}$ for small values of r and to $\lambda_{15} r^{-15}$ for large values of r , can easily be devised. This is the case for the law

$$f = \frac{\lambda_{15} r^{-15}}{1 + a^6 r^{-6}},$$

provided a be given a suitable value.

* This statement, if true, raises the question whether one is justified in summing over all atoms of a crystal as has been done throughout this paper. However, the main part of the *crystal potential constants* represents the effect of neighbouring atoms (*e.g.*, $C_{10} = 12.3112$, as compared with 12 if all except neighbouring atoms are neglected), and further

in calculating crystal distances, expressions of the type $C_n \frac{1}{r^{n-1}}$ occur, so that little error is introduced. Furthermore, the distant atoms will exercise *some* effect, though small, and it is questionable whether it is more accurate to *neglect* it altogether than to calculate it on the basis of the same repulsive law as applies at small distances.

† For limits of error of force constants see Paper II, p. 472, 475; Paper IV, p. 163.

§ 12. *Summary.*

Methods are given of obtaining the forces between certain neon-like and argon-like ions. These are used with success to account for the observed distances in certain crystals of the rock-salt type. They can also be used to make predictions of crystal constants not yet measured.

The values of compressibility, elasticity, and other constants of the same crystals are also calculated and compared when possible with experiment.

The conclusion is that the repulsive force of neon-like ions *in crystals* can well be represented by an inverse 11th-power law and that of argon-like ions by an inverse 9th-power law. Reasons are given for supposing that the latter law is not adequate over all distances, but that for large distances a better approximation is the inverse 15th power.

On the Construction of a Standard High-frequency Inductive Resistance and its Measurement by a Thermal Method.

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1. *Introduction.*

The ordinary methods of measuring the radio-frequency resistance of inductance coils depend on the measurement of the resistance of a complete circuit, containing, usually, the coil, a thermo-ammeter, a condenser and leads. The lack of knowledge of the effective resistance of the circuit outside the coil, of the losses induced in the surrounding objects, and of the distribution of parasitic currents, leave some doubt on the reliability of the value of the resistance obtained by these methods. To obtain reliable measurements it is necessary to fall back on some thermal method by means of which the power lost in the coil itself can be measured quite independently of the circuit and neighbouring bodies. The method described in this paper was carried out essentially as a check to the usual methods of measurement.

A number of investigators have used thermal methods to measure the effective resistance of coils. Amongst them may be mentioned T. P. Black, L. W. Austin, H. Abrahams, G. W. O. Howe, and L. Lehrs. T. P. Black (1)

compared the effective resistance of long solenoids with the effective resistance of straight wires, employing a method resembling that of J. A. Fleming (2) for measuring the high-frequency resistance of straight wires by means of a differential air thermometer. L. W. Austin (3) compared the heat given out by a coil when current at radio frequencies and direct current were passed through two similar coils. The coils were immersed in oil, and the equality of temperature noted by thermo-junctions connected in opposition in the two vessels. H. Abrahams (4) compared the rise of temperature of coils after passing radio-frequency current and then direct current by quickly finding the change in the direct-current resistance measured by a Wheatstone bridge. G. W. O. Howe (5) found the rise of temperature of long solenoids by means of a thermo-junction placed near the centre, and compared the effect of direct and high-frequency currents. He thus assumed that the loss is uniformly distributed along the coil, an assumption which will hold only if the coil is long. L. Lehrs (6) enclosed the coil in a vessel connected to a very sensitive manometer, and adjusted the alternating and direct currents so that no change could be observed on switching from one to the other.

The differential methods are liable to error through the difficulty of obtaining absolutely similar vessels. In methods that require the coil to be enclosed in a vessel, a necessary condition for sensitivity is that the heat capacity of the vessel should be small, which necessitates a compact coil and preferably one of not too low a resistance. This is not suitable for comparing methods of measurement, for if the coil is small some of the parasitic currents will become small; thus, one of the possible sources of error would be eliminated. Also the main difficulty arises in the measurement of low resistance coils.

It is therefore necessary to devise a thermal method which will allow the absolute measurement of the high-frequency resistance of a low-resistance coil of comparatively large dimensions without the use of too big a current. This last point is important, for, although methods using large currents repeat to an accuracy of about 1 per cent., it is difficult to ascertain the absolute value of these large currents when dealing with frequencies of 1,000 kilocycles or higher. An instrument may compare accurately two currents of the same frequency, but may be in error when comparing a large current at radio-frequency with direct current.

2. Principle of Method.

In the method described here the coil acts as its own thermometer, which is sufficiently sensitive to allow accurate measurements to be made when the energy dissipated in the coil is only of the order of one watt. The method

depends on the expansion of mercury in a glass tube bent into the form of a coil when first high-frequency current and then direct current is passed through the coil.

If I_1 is the high-frequency current, which produces the same thermal effect as the direct current I_0 , the ratio of the high-frequency resistance R_1 to the direct-current resistance R_0 is given by

$$R_1/R_0 = I_0^2/I_1^2.$$

Two glass coils were made and filled with mercury. One end of each coil was closed by a stopcock, and the other terminated in an open capillary tube. The current was led in through platinum wires fused into the glass. Two reading microscopes were focussed on to two marks on the capillary tube, and the time taken for the mercury column to move from one mark to the other was taken with a stop-watch. The watch was initially tested against a standard clock and found accurate.

It is evident that the coil as a whole acts as a thermometer, so that the temperature of the mercury is absolutely definite, when it stands at either of the fixed points on to which the microscopes are focussed, irrespective of the temperature of the surrounding air.

Suppose t_1^0 , t_2^0 and t_0^0 be the temperatures corresponding to the upper mark, the lower mark and the surrounding air respectively. Let τ_H secs. be the time of heating and τ_C secs. that of cooling of the mercury column from one mark to the other. Then the differential equation during heating is

$$M \frac{dt}{d\tau} = Q - k(t - t_0) \quad (1)$$

where M is the thermal capacity of the coil, Q the quantity of heat generated in the coil per second when the current is flowing, and k is the loss of heat per second per degree difference with the surrounding air.

Integrating equation (1) and putting the conditions that $t = t_2$ when $\tau = 0$, and $t = t_1$ when $\tau = \tau_H$, we have

$$\frac{Q - k(t_1 - t_0)}{k(t_1 - t_2)} = \frac{1}{e^{K\tau_H} - 1} \quad (2)$$

where $K = k/M$.

During cooling, $Q = 0$, and we must write $-\tau_C$ for τ_H in equation (2), and thus obtain

$$\frac{t_1 - t_0}{t_1 - t_2} = \frac{1}{1 - e^{-K\tau_C}}. \quad (3)$$

Eliminating t_0 from equations (2) and (3), we have

$$\frac{2R}{k(t_1 - t_2)} \cdot I^2 = \coth \frac{K}{2} \tau_H + \coth \frac{K}{2} \tau_C, \quad (4)$$

in which $I^2 R$ has been substituted for Q , I being the r.m.s. of the current entering the coil and R the resistance of the coil.

I shall denote the right-hand side of this equation by P , so that we have

$$\frac{2R}{k(t_1 - t_2)} I^2 = P. \quad (5)$$

From equation (4) we see that, by plotting P against I^2 , a straight line passing through the origin should be obtained. This straight line is independent of the air temperature, which can, therefore, vary so long as it remains constant over the period required to take the time of heating and the time of cooling.

To evaluate K .—In order to calculate the value of P from τ_H and τ_C it is necessary to find the value of K . Two methods become at once evident. If we turn to equation (3) we can write it in the form

$$K\tau_C = \log_e \frac{t_1 - t_0}{t_2 - t_0}. \quad (6)$$

Since the coil behaves as a thermometer, by measuring the height of the mercury above a fixed plane before heating (that is when the temperature of the coil could be thought to be equal to that of the surrounding air), and knowing the heights h_1 and h_2 respectively of the two marks on the capillary tube, we can calculate $(t_1 - t_0)/(t_2 - t_0)$ from the relation:—

$$\frac{h_1 - h_0}{h_2 - h_0} = \frac{t_1 - t_0}{t_2 - t_0}.$$

Hence, by finding τ_C we ought to be able to find K . A few measurements soon led to the conclusion that it was exceedingly difficult to make the temperature of the coil, which behaves as an exceedingly sensitive thermometer, accurately equal to that of the air. The method was, therefore, abandoned.

The second method consisted in finding the time τ_1 of cooling from the upper mark to the lower, and the height h_3 of the level of the mercury after the coil had cooled for a further time τ_1 .

From equation (5) we have

$$K\tau_1 = \log_e \frac{t_1 - t_0}{t_2 - t_0} \quad \text{and} \quad K\tau_1 = \log_e \frac{t_2 - t_0}{t_3 - t_0}.$$

Eliminating t_0 , we have

$$K\tau_1 = \log_e \frac{t_1 - t_2}{t_2 - t_3}.$$

Although this method gave more consistent results than the first, the values obtained could only be used as a guide in the determination of K .

Eventually K was more accurately determined by finding the value, which gave a straight line passing through the origin, for the relation between P and I^2 for direct current. By using this value for the high-frequency current, the lines obtained also passed through the origin, showing that the error in K could not be large. This method of estimating K is not as tedious as one might expect, for its value need not be very accurate, as will be explained later.

3. Construction of the Coils.

Two mercury coils, numbered I and II, were made.

Coil I.—This coil was made of glass tubing 0.5 cm. internal diameter and 0.65 cm. external diameter. It was built in the form of a single-layer coil of square cross-section, with $8\frac{3}{4}$ turns of side varying from 10 to 12 cms. and an average pitch of 0.9 cm. The turns were held together by melting paraffin wax on the top and bottom sides of the coil. The capillary tube had a diameter of about 0.03 cm. The distance between the two marks was approximately 2 cms. The whole coil was supported in a wooden box on paraffin wax block. The box was fitted with a lid, through which the tap and the capillary tube were allowed to pass. The holes were stopped with cotton-wool to prevent the circulation of air.

Coil II.—This coil was of similar construction, but bigger than coil I. It had $14\frac{3}{4}$ turns of side varying from 16 to 16.5 cms., the average pitch being 1.53 cms. The internal diameter of the glass tube was 0.7 cm. and the external 0.8 cm. The bore of the capillary tube was 0.056 cm. in diameter. The distance between the two marks was approximately 3.5 cms. This coil was also placed in a wooden box, but owing to its weight it had to be supported on a block of wood.

4. Precautions.

(a) *Capillary Tube.*—The size of the capillary gave some difficulty at first, for though the coils were thoroughly cleaned with ether, alcohol and water, and subsequently dried, the mercury (specially purified for the purpose) did not rise and fall uniformly in the capillary tube after the coil had been used for about a day. This was presumably due to moisture entering the capillary tube. By choosing a sufficiently wide tube, however, the error caused by this irregular motion became negligible.

(b) *Variation of Air Temperature.*—The main difficulty encountered was due to variations in the temperature of the room. This was kept as constant as

possible by keeping doors and windows closed. The first few results were not consistent; the reason was soon found to be due to the glass taking considerable time to reach a temperature near the working temperature of the mercury (corresponding to the two marks on the capillary tube). It was found necessary to keep the mercury at a level between the two marks for two or three hours before taking a series of readings, thus allowing the glass to reach the necessary temperature. This effect is probably caused not only by the expansion of the glass, but also by the increased rate of cooling of the mercury when in contact with the colder glass. It is probably for this same reason that discrepancies were found in the values of K obtained by the methods described above.

Owing to variations in the rate of cooling of the mercury, due to changes of the air temperature, the time of cooling was taken before and after heating. If τ_C and τ_C' are the times of cooling before and after heating respectively, the value of P was taken to be

$$P = \coth \frac{K}{2} \tau_H + \frac{1}{2} \left[\coth \frac{K}{2} \tau_C + \coth \frac{K}{2} \tau_C' \right]. \quad (7)$$

It might be supposed that more accurate values of P could be obtained by making $\coth \frac{K}{2} \tau_H$ large compared to $\coth \frac{K}{2} \tau_C$; that is, by making τ_C larger than τ_H . Experience showed, however, that if τ_C was too large, the time over which a reading was taken became so long that the temperature of the room varied appreciably, so that the mean value obtained for $\coth \frac{K}{2} \tau_C$ did not represent the true value of $\coth \frac{K}{2} \tau_C$ during the period of heating.

The total time of one heating and one cooling can be shown to be a minimum when $\tau_C = \tau_H$. Hence the most reliable results would be expected to occur when τ_C was greater than τ_H , but not excessively greater. For the same reason the reliability is decreased if the distance between the two marks on the capillary tube is too great, for the time taken over one reading becomes too long.

(c) *Measurement of Current.*—The direct current was taken from a 4-volt battery through a rheostat, and the current measured on a potentiometer. The current was kept constant during the time of heating by varying the fine adjustment of the rheostat. In this way the current was never allowed to vary by more than 1 part in 1,000.

The high-frequency current was measured by a non-contact thermo-ammeter.

The heater used with coil I was a 3-cm. length of No. 46 s.w.g. copper wire rolled out to 0.01 mm. thickness. That used with coil II was No. 44 s.w.g. copper wire rolled out to 0.01 mm. thickness. The thermo-ammeter and galvanometer were calibrated with direct current.

Owing to the size of the high-frequency current (about 1 amp.), the current density in the heater was high. Now, at these high-current densities the square law of the deflection of the galvanometer with current no longer holds, but, over the small range used, the curve connecting deflection and the square of the current was a straight line, though not passing through the origin. The thermo-ammeter was exceedingly quick in action when the current density was high, so that there could be no doubt about the zero reading.

The reading of the galvanometer was taken every 30 seconds for the high frequency current and the mean value taken. The zero was checked after each reading. The oscillator used was very constant, the maximum variation of current over any one set of readings being 0.7 per cent., the average being less than 0.2 per cent.

(d) *The self-capacity of the coils.*—In the experiments, the e.m.f. was induced directly into the coil. If the coil is assumed to consist of a self-inductance L , in series with a resistance R , with a condenser C in parallel, the current measured by the thermo-ammeter is less than the current passing through the inductance and resistance.

It can easily be shown that, if the frequency is not near the natural frequency of the coil, the apparent effective resistance R' measured by the thermal method is given by

$$R = R'(1 - 2LC\omega^2). \quad (8)$$

5. Sources of Error.

In this method of measuring the effective resistance of the mercury coils the following assumptions are made.

(a) *Law of cooling.*—It is assumed that Newton's Law of Cooling holds. Since the distance between the two marks on the capillary represented a change of about $\frac{1}{2}^\circ \text{C.}$, and the temperature of working was of the order of 2°C. above the temperature of the room, it is evident that the error from this assumption is quite negligible.

(b) *The thermo-ammeter.*—The thermo-ammeter was calibrated for direct current. It was therefore assumed that the same calibration held for the high-frequency current. This assumption cannot give any appreciable error, since

the heaters, which were not in contact with the thermo-junctions, were made of strips of 0.01 mm. thickness.

(c) *Losses in box.*—For comparison with the ordinary methods of measurements described in Part I, it was assumed that the wooden box, in which the coils were placed, produced no loss. This was tested by inserting a piece of similar wood inside the coil. Although this affected the tuning slightly by altering the self-capacity of the coil, on returning the current returned to its original value, showing that the wood produced no appreciable loss.

(d) *Heat distribution.*—The heat distribution in the coil is different for high-frequency current and direct current. There are two causes for this, the dielectric loss in the glass at high frequencies and the greater loss that occurs in the end turns compared to the centre turns in any coil at high frequency.

(i) The dielectric loss was kept small by using as thin glass tubes as possible. It should be noticed also that, owing to the large size of the conductor, the potential gradient at the glass is not large.

E. Schott (4) has measured the angle of loss of a number of glasses at 500 metres, and obtained values varying from 1.39 to 22.6 minutes at ordinary air temperature, the values remaining very constant with change of frequency.

A condenser of 20 micro-microfarads capacity, which is the order of the self-capacity of the coils, made of glass having an angle of loss of 20 minutes, would have an equivalent series resistance of approximately 0.01 ohm, at a frequency of 1,000 kilocycles. Evidently the error due to the loss in the glass is negligible, and the dielectric loss of the paraffin wax will produce a very much smaller effect.

(ii) Owing to the main magnetic fields of the coils, more energy is wasted in the end turns than in the centre turns. It is safe to assume, however, that over the temperature range of working the expansion of the mercury is proportional to the change of temperature. Then, if various parts of the tube are at different temperatures, the total volume of the mercury will be the same as if the temperature were uniform and equal to the mean temperature of the tube.

Again, since the loss of heat is proportional to the difference of temperature between any portion of the tube and the surrounding air, any difference of temperature between one portion of the box and another will have no effect. One portion of the tube may lose heat faster than another, but the total loss of the whole tube depends on the mean temperature of the air surrounding the tube.

Owing to unavoidable irregularities, it is possible that the value of K differs for the various portions of the coil. In this case the value of K for the whole

coil would be different for high-frequency and for direct current on account of the different distribution of heat. That this is not so is well shown by the accuracy with which the straight lines obtained by plotting P against I^2 pass through the origin. (Figs. 1 and 2.)

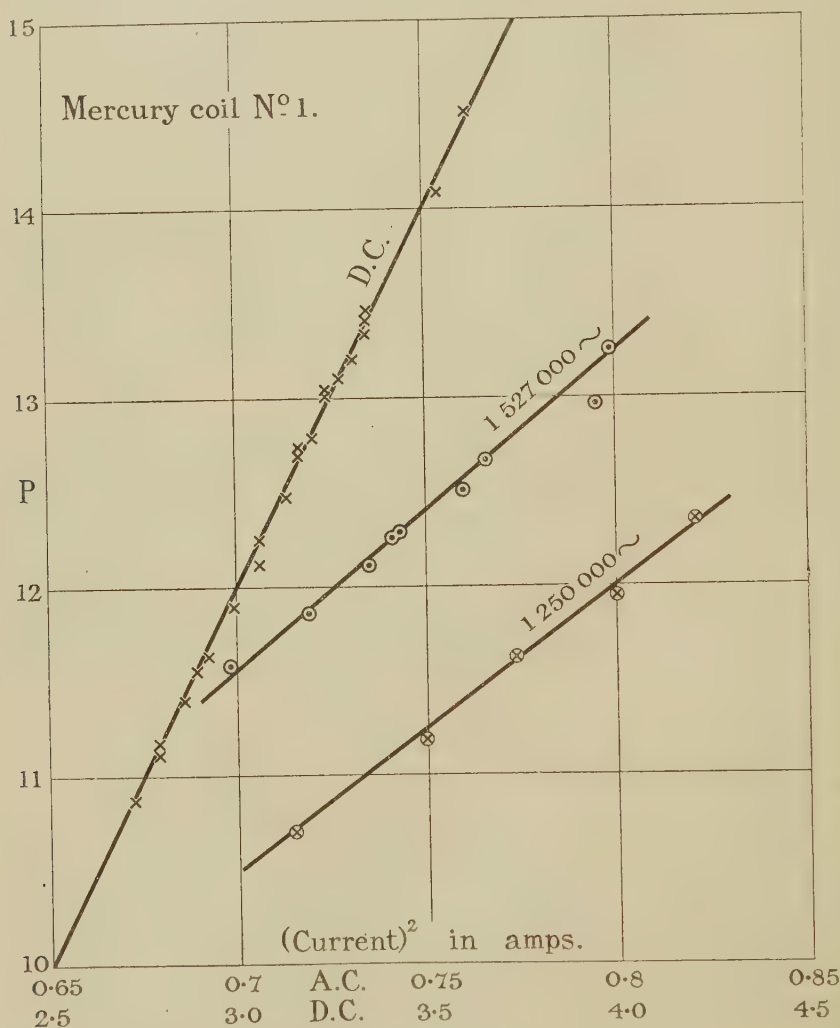


FIG. 1.

(iii) Owing to the different distribution of heat explained above it was not possible to take high-frequency and direct-current readings alternately. A period of about one hour was required to allow the glass to return to a steady state. It was therefore necessary to verify the constancy of K . This was done

by taking readings for direct current on different days. The results agreed, showing that the value of K had not altered.

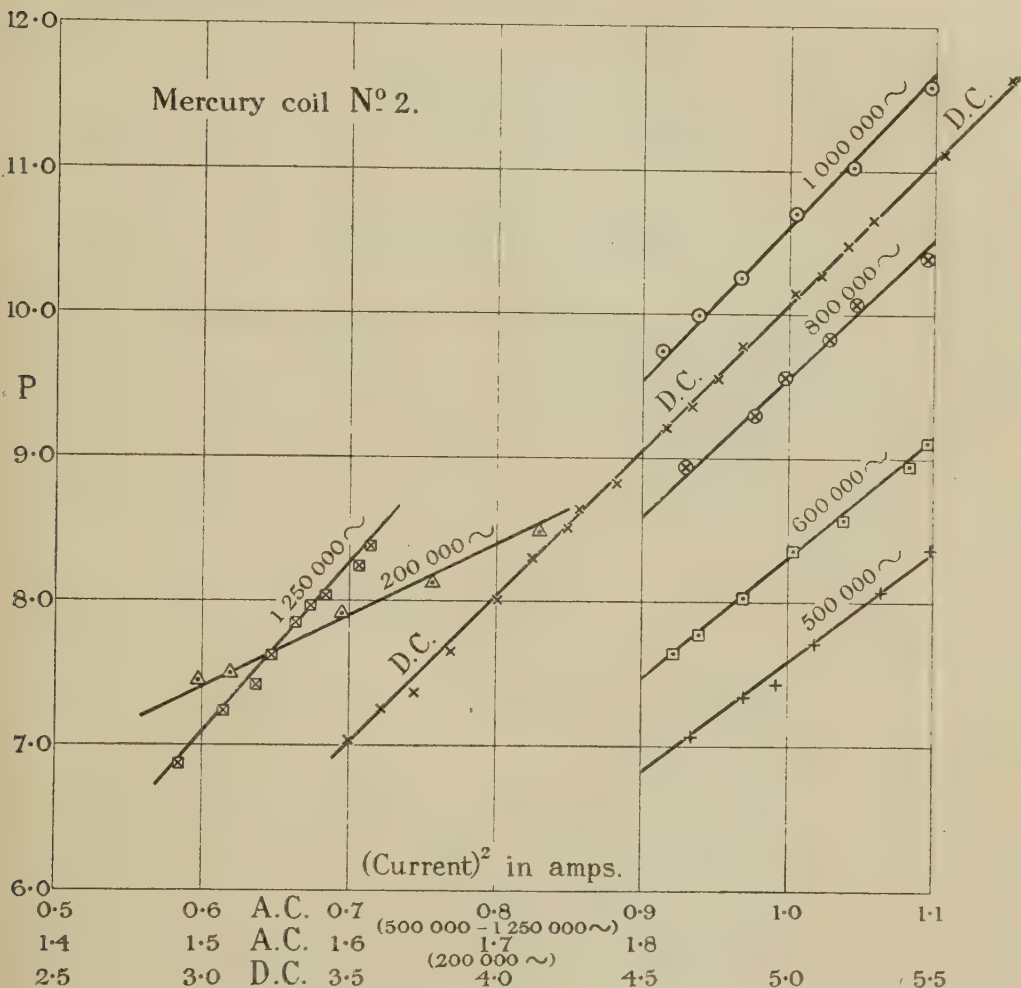


FIG. 2.

6. Accuracy of Method.

The accuracy of the method depends largely on the accuracy with which the value of K can be determined. Returning to equation (4) we have

$$P = \coth \frac{K}{2} \tau_H + \coth \frac{K}{2} \tau_C,$$

therefore

$$-\frac{\delta P}{P} = \frac{\delta K}{K} \cdot \frac{\alpha_H (\coth^2 \alpha_H - 1) + \alpha_C (\coth^2 \alpha_C - 1)}{\coth \alpha_H + \coth \alpha_C},$$

where

$$\alpha_H = \frac{K}{2} \tau_H \quad \text{and} \quad \alpha_C = \frac{K}{2} \tau_C.$$

Since α_H and α_C lie between 0.1 and 0.5, by expanding we can neglect third and higher powers of small quantities. This becomes

$$-\frac{\delta P}{P} = \frac{\delta K}{K} (1 - \frac{2}{3} \alpha_C \cdot \alpha_H),$$

in which the product $\alpha_C \cdot \alpha_H$ varied between 0.02 and 0.20, the average value being about 0.04.

We can test the accuracy with which K is estimated by seeing how accurately the points obtained by plotting P against I^2 in any one set of readings lie on a straight line for different values of the product $\alpha_C \cdot \alpha_H$; for, if this product were constant, the percentage error in P would also be constant, and the points would still lie on a straight line.

If P, R, I , etc., and P', R', I' , etc., represent the values for direct and alternating currents respectively, we have for a small error in K

$$\frac{R'I'^2}{RI^2} = \frac{P'}{P},$$

therefore

$$\frac{\delta R'}{R'} = \frac{RI^2}{I'^2} \cdot \frac{\delta P'}{P'} \cdot \frac{P}{\delta P} = \frac{RI^2}{I'^2} (1 - \frac{2}{3} \alpha_C' \cdot \alpha_H' + \frac{2}{3} \alpha_C \cdot \alpha_H).$$

If $\alpha_C \alpha_H = \alpha_C' \alpha_H'$, there would be no error in R' due to an error in K . Hence the accuracy in estimating the effective resistance will depend on the closeness of the value of $\alpha_C \cdot \alpha_H$ for direct and alternating currents. Incidentally, since $\alpha_C \cdot \alpha_H$ is never large, K need not be obtained to a great degree of accuracy, and what appears a tedious process of finding the best value of K which will make the direct-current line pass through the origin is, in reality, fairly simple, when an approximate value of K has been found by experiment, as explained above.

The accuracy in estimating the effective resistance will thus depend on the closeness of the value of $\alpha_C \cdot \alpha_H$ for the direct and alternating currents, and will be of the same order of accuracy as that of K . That is, the accuracy with which the best straight line can be drawn through the points over as wide a range of the value of $\alpha_C \alpha_H$ as possible.

For coil I the value of $\alpha_C \alpha_H$ varied from 0.02 to 0.04, and for alternating current this was 0.025 to 0.04. For coil II the range was 0.03 to 0.20 for direct current and 0.04 to 0.10 for alternating current.

An examination of the lines of figs. 1 and 2 will show that the error in drawing

the mean straight line through the points is less than 1 per cent., which we can take to be the approximate inaccuracy of the method.

7. *Experimental Results.*

The effective resistance was found for coil I at two frequencies, namely, 1,250 and 1,527 kilocycles per second. The measurement of K gave values ranging from 0.0015 to 0.0018. From the values of P obtained with direct current, K was eventually found to be 0.0016. In Table I is given a specimen of a series of readings taken at high frequencies.

Table I.—Coil I at a frequency of 1,527 kcs. per sec.

Date.	Mean Current. (Amps.)	τ_0 Seconds. (Before heating.)	τ_H Seconds.	τ_0 Seconds. (After heating.)	P.
August 21	0.795	275.4	147.3	298.4	12.97
" " " "	0.766	395.0	132.0	425.4	12.67
" " 22	0.799	267.4	144.5	291.5	13.25
" " " "	0.760	365.9	136.9	406.8	12.52
" " 23	0.698	156.0	324.0	174.1	11.58
" " 25	0.743	203.4	200.7	220.0	12.29
" " " "	0.741	249.2	168.0	284.3	12.26
" " " "	0.719	475.0	137.5	486.3	11.86
" " " "	0.735	437.4	136.0	446.6	12.12

Similar tables were obtained for the other frequency and for direct current, the latter covering a much larger range and including 38 readings, many readings for the same current giving accurate repetition of the values previously obtained. The readings are shown plotted in fig. 1. All the straight lines obtained pass accurately through the origin.

The measurements on coil II were made at six different frequencies, ranging from 200 to 1,250 kilocycles. The results are shown by the straight lines of fig. 2. Here again it will be noticed that all the lines produced pass accurately through the origin.

From the lines of figs. 1 and 2 the effective resistance of the coils was calculated. The result is shown in Table II, in which the correction for the self-capacity of the coil has been applied.

The values for coil II are plotted against the square root of the frequency in fig. 3. This form of plotting was chosen so as to obtain a flat curve so that any small deviation from the curve would be more noticeable. It will be seen, however, that the curve is perfectly smooth.

Table II.

Coil.	Frequency. (Kilocycles per second.)	Effective Resistance. (In ohms.)
No. 1	1,527	0.98 ₉
"	1,250	0.90 ₈
"	Direct current	0.242
No. 2	1,250	1.41 ₂
"	1,000	1.29 ₂
"	800	1.17 ₈
"	600	1.03 ₅
"	500	0.95 ₂
"	200	0.62 ₄
"	Direct current	0.254

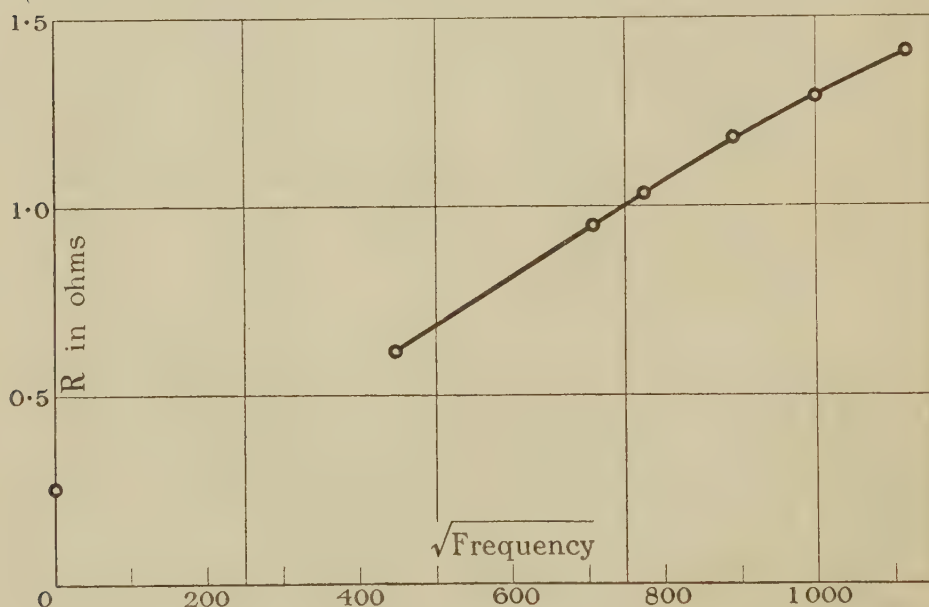


FIG. 3.

8. Comparison with Resistance Variation Method of Measurement.

Two forms of the resistance variation method of measurement were used. In method I the resistance of a circuit was measured, and from this was subtracted the effective resistance of the leads and heater, the air condenser used being assumed to have negligible resistance.

In method II the circuit contained a second coil into which the e.m.f. was induced. The resistance of the coil was taken to be that of the difference in the resistance of the circuit with and without the mercury coil.

The results compared with the thermal method are given in Table III, in which the correction for self-capacity is applied.

Table III.

Coil.			Effective Resistance Measured by—		
			Method I.	Method II.	Thermal Method.
No. 1		1,527	0.99	0.99	0.98 ₉
"		1,250	1.09	0.91	0.90 ₈
No. 2		1,250	1.49	1.41	1.41 ₂
"		1,000	1.34	1.29	1.29 ₂
"		800	1.19	1.18	1.17 ₈
"		600	1.07	1.04	1.03 ₈
"		500	0.97	0.96	0.95 ₂
"		200	0.62	0.62	0.62 ₄

In order to show that changing the condenser reading had a negligible effect on its effective series resistance, the resistance of a circuit was measured by method I, with first coil I and then coil II, the same variable air condenser being used. The frequency was 1,250 kilocycles.

The difference in resistance was 0.61 ohm, which agrees absolutely with the difference of the resistance of the two coils by the thermal method after the necessary correction for self-capacity and leads have been applied.

9. Conclusion.

Calorimetric or thermal methods must for the present be the basis of all high-frequency resistance measurements. From the results it appears that the thermal method of measurement described gives an accuracy well within 1 per cent., with a dissipation of energy of the order of 1 watt. The mercury coils could therefore be used as standards for comparing the various methods of resistance measurement.

By using double-walled boxes to hold the coils and packing the interspace with ice, the accuracy of the readings could probably be considerably increased, but since, at present, the accuracy with which high-frequency current can be measured is only of the order of $\frac{1}{2}$ per cent., this was not considered necessary.

The method could probably be used to check the formulæ for the effective resistance of conductors of simple shape. Unfortunately, the difficulty of bending glass tube accurately to shape prevents the formulæ for the effective resistance of coils being checked directly from the thermal measurements of the mercury coils.

The comparison of the results obtained with the variation of resistance method, which was the fundamental reason for which the work was undertaken, show absolute agreement with method II, but gives a small discrepancy with method I. For low-resistance coils, then, method II would appear to be preferable. The discrepancy of method I is, however, quite small, and would probably be negligible for coils having a higher resistance.

In conclusion, my thanks are due to the Radio Research Board of the Department of Scientific and Industrial Research, and to its Committee on the Propagation of Waves and Radio Standards, under whose auspices the work was carried out, and for the kind criticism of their members.

I also wish to thank Mr. D. W. Dye for general criticism and advice while the work was in progress. Also Messrs. Pratt and Oliver for the care with which they took some of the measurements.

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The Flame Spectra of Carbon Monoxide and Water Gas
Part II.

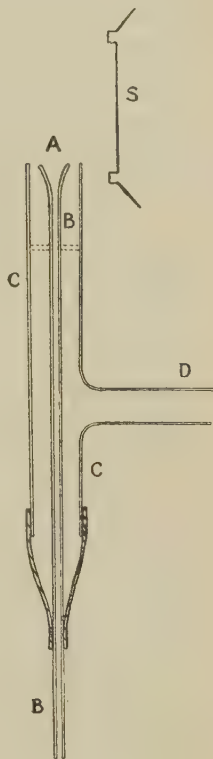
By FRANK R. WESTON, B.Sc., D.I.C.

(Communicated by Prof. W. A. Bone, F.R.S.—Received July 30, 1925.)

[PLATE 10.]

Since making my previous communication* to the Society upon the Flame Spectra of Carbon Monoxide and Water Gas, I have, at Prof. Bone's suggestion, carried out some further experiments in which flames of carbon monoxide, hydrogen, or mixtures of the two in determined proportions, were maintained in an atmosphere rich in oxygen, immediately in front of the slit of the spectrograph without any quartz window or the like intervening, whereby I was able to obtain a much better illumination of the slit and more intensive spectrograms of the flames. The results of these further experiments have confirmed and extended in so striking a way the conclusions about the mechanism of CO-combustion which were set forth in my previous paper, that it has been decided to describe them in this further communication.

The new procedure adopted in these experiments will be understood by reference to the accompanying diagram. A jet of the combustible gas was ignited as it issued from the expanded orifice A of the 1 mm.-bore quartz tube BB. This orifice had been previously expanded in the oxy-hydrogen blowpipe until it had acquired the particular form shown in the diagram. The quartz tube was suitably mounted co-axially with a wider glass tube CC (internal diam. 8 mm.), having a side-arm D, through which a stream of oxygen was maintained. The flame at the orifice A was thus surrounded by an atmosphere of oxygen; and by placing the burner at a distance of about 1 cm. from the slit S of the Bellingham and Stanley spectrograph (wave-length range 6000 Å.U. to 2100 Å.U.), much more intensive spectrograms were obtained for oxy-



* 'Proceedings,' A, vol. 108, p. 176 (1925).

carbon monoxide and oxy-hydrogen flames than by the method previously employed. In each case the undried combustible gas, stored over a mixture of equal volumes of glycerine and water, was burnt at a constant rate of 10 litres per hour; and a 45 minutes exposure was allowed in taking the spectrograms, Imperial Ordinary plates being used.

A selection of the spectrograms so obtained is shown in the accompanying Plate 10: in making these reproductions from the original negatives the exposures used were in all cases the same, viz. 20 seconds, in an enlarging lantern with a 60-watt lamp as the illuminant.

No. 1, which was obtained from a flame of pure (undried) carbon monoxide, shows a very strong continuous spectrum extending far into the ultra-violet (certainly up to 2200 Å.U.), its intensity being such that the characteristic CO-bands in the region 5500 to 3900 Å.U., observed in my previous experiments, were now completely masked. On the other hand, the broad bands which had been previously noticed in the region 2800 to 2300 Å.U. of the spectrogram of a CO-"ozonised"-oxygen flame were now brought out rather more distinctly. The intensity of this CO-oxygen continuous spectrum almost masks the CO-OH₂ "steam lines," which are now only faintly visible. No. 5 is the spectrogram obtained from a flame of pure undried hydrogen burning in an envelope of oxygen; the normal "steam lines" are shown much intensified.

In Nos. 2 to 4 inclusive are shown in a very striking way the effects of gradually adding hydrogen to the burning gas, until the equimolecular "water-gas" mixture is reached. It will be seen that in confirmation of my previous results (*q.v.*) such addition of hydrogen immediately caused a marked and rapid diminution both in the range and intensity of the continuous CO-oxygen spectrum, until, with the "water-gas" equimolecular mixture (No. 4), it had practically all disappeared, leaving only the CO-OH₂ steam lines visible in the print. It should, however, be stated that in the original negative vestiges of the continuous CO-oxygen spectrum can be seen in the region 4300 to 3300 Å.U., though in the print they are hardly visible at all.

In order to ascertain whether the addition of a certain volumetric proportion of steam to the burning carbon monoxide would have any appreciably different effect upon the flame spectrum from that produced by the addition of the same volumetric proportion of hydrogen, I next took spectrograms of the flame of carbon monoxide saturated with steam in the one case at 50° and the other at 75° C. respectively, the barometric pressure being about 763 mm. in each case. The gas burnt would thus contain in the one case

about 12 per cent. and in the other about 38 per cent. of steam respectively. On subsequently comparing the spectrogram (No. 6) obtained by burning CO containing 12 per cent. of steam with that (No. 2) obtained by burning CO containing 12 per cent. of hydrogen, no material difference between them could be detected. On the other hand, the addition of 38 per cent. of steam (No. 7) seemed to have little more effect than the addition of only 22 per cent. of hydrogen (No. 3).

That the observed effects upon the continuous and banded parts of the CO-flame spectrum of adding either hydrogen or steam to the burning gas were not due to a mere physical adsorption of such radiation by steam was proved in the next experiment, in which a hydrogen flame was interposed between the pure CO flame and the slit of the spectrograph, so that the radiation emitted by the burning carbon monoxide had to pass through the hydrogen flame before entering the spectrograph. No difference, however, could be detected between the resulting spectrograph (No. 8) and that (No. 1) obtained when the same CO flame was burnt without any interposition of a hydrogen flame between it and the slit of the spectrograph. This shows that a hydrogen flame is quite transparent to that part of the radiation from a CO flame which produces the characteristic continuous part of its spectrum.

In Nos. 9 and 10 are reproduced the spectrograms obtained from flames of equimolecular mixtures of CO and H_2 and of CO and N_2 respectively. Exactly the same volume of CO was burnt in the 45 minutes duration of each of the two experiments, but it was diluted in the one case with its own volume of hydrogen and in the other with nitrogen; otherwise the conditions were all the same. The unmistakable difference here shown between the two spectrograms in question proves that the suppression by hydrogen (and/or steam) of the continuous part of the CO-flame spectrum in the case of the "water-gas" flame is no mere diluent effect. Presumably, therefore, it is due to the supersession of the CO-oxygen by the CO-steam interactions in the flame.

Prof. Bone, under whose supervision these experiments were carried out, considers that the results thereof strengthen the conclusion put forward at the end of my previous paper, namely, that in the flame of pure (undried) carbon monoxide, two sets of independent interactions occur simultaneously, namely: (a) direct interactions between carbon monoxide and oxygen, exciting radiations which give rise to the continuous and banded parts of the spectrum, and to the characteristic blue colour of the flame, and (b) interactions between CO and OH_2 molecules, which originate the "steam lines" in the spectrum. When hydrogen is gradually added to the burning gas

the relative proportions of the first-named interactions diminish rather rapidly and proportionately more of the CO is burnt by interaction with OH_2 -molecules, until when an equimolecular mixture of carbon monoxide and hydrogen is reached, the CO-steam interactions occur to the practical exclusion of the CO-oxygen interactions.

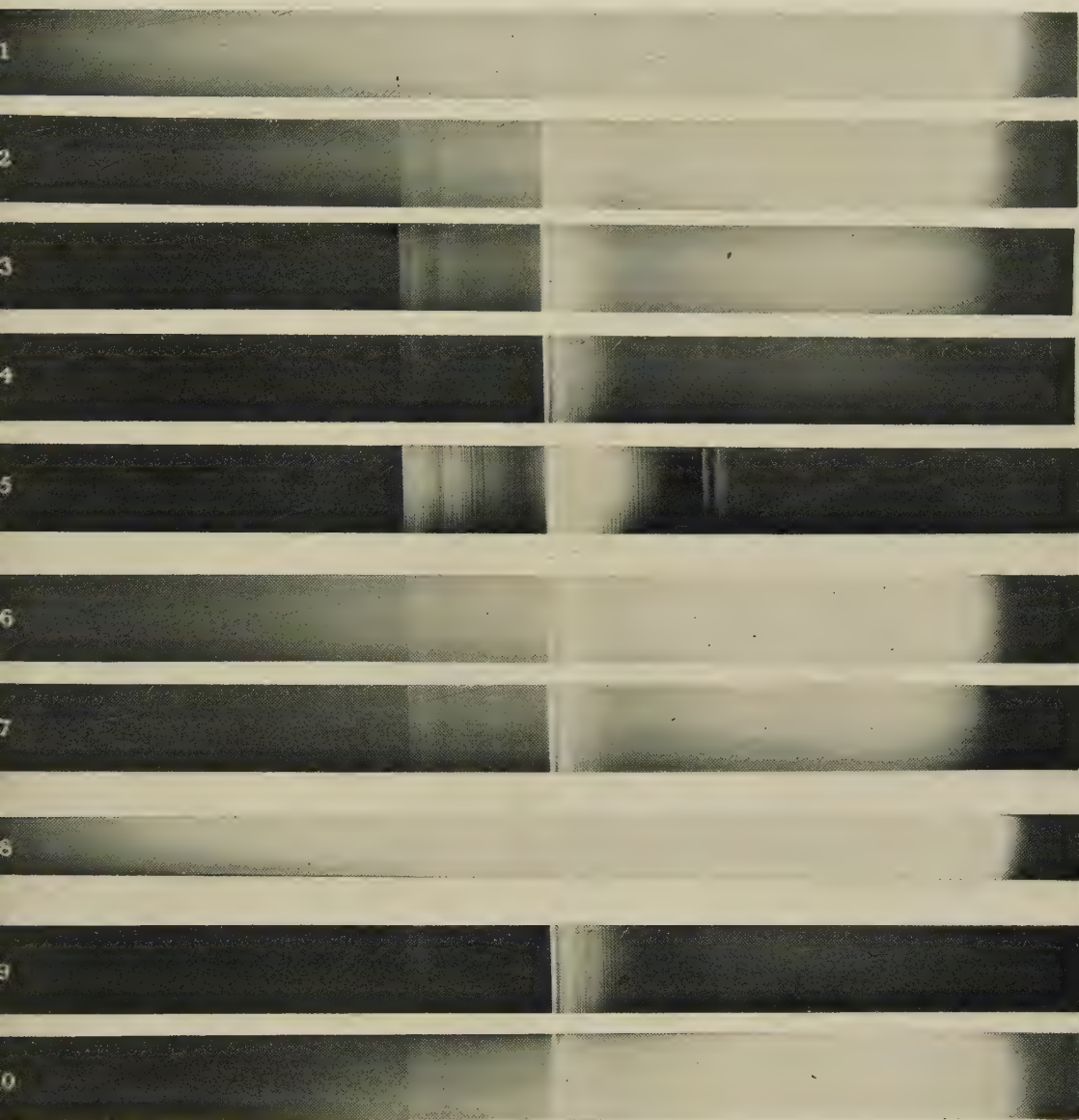
In conclusion, I desire to express my indebtedness to the Gas Light and Coke Company of London, the tenure of whose Gas Research Fellowship at the Imperial College of Science and Technology, South Kensington, has enabled me to carry out this research.

The Thermal Decomposition of Nitrogen Pentoxide at Low Pressures.

By HERBERT SIM HIRST and ERIC KEIGHTLY RIDEAL.

(Communicated by Sir W. J. Pope, F.R.S.—Received 22nd August, 1925.)

Unimolecular reactions possess a unique interest in that, as Perrin ('Ann. Physique,' vol. 11, p. 5, 1919) first pointed out, for the occurrence of such, some type of interaction between radiation and matter must take place. Although such reactions appear to be extremely rare, many physical processes such as evaporation, ionisation in gases at high temperatures and radio-active decay, proceed at rates conforming to a unimolecular law; true chemical reactions which are definitely unimolecular and not pseudo-unimolecular in character are, on the other hand, stated by many (*e.g.*, Lowry, 'Trans. Farad. Soc.,' vol. 17, p. 596 (1922)) to be non-existent. In order to substantiate this statement, it is clearly necessary to prove the more complex character of any reaction which satisfies the usual criteria of unimolecular change. The thermal decomposition of gaseous nitrogen pentoxide apparently fulfils these conditions, for Daniels and Johnston ('J. Am. C. S.,' vol. 43, p. 53 (1921)) showed that the reaction proceeded according to a unimolecular law over wide ranges of variation of pressure, and Lueck (*ibid.*, vol. 44, p. 757 (1922)) obtained practically identical unimolecular constants for the decomposition in solution in carbon tetrachloride and chloroform. On the other hand, Daniels, Wulf and Karrer (*ibid.*, vol. 44, p. 2402 (1922)) suspected the reaction to be autocatalytic,



1 Carbon monoxide.

2 { CO 88 p.c.
H₂ 12 p.c.

3 { CO 78 p.c.
H₂, 22 p.c.

4 { CO 53 p.c.
H₂ 47 p.c.

5 Hydrogen.

6 CO with 12 p.c. steam.

7 CO with 38 p.c. steam.

8 CO flame spectra with H₂
flame absorption.

9 { CO 53 p.c.
H₂ 47 p.c.

10 { CO 51 p.c.
N₂ 49 p.c.

owing to the apparent retardation of the reaction velocity in the presence of ozone, but the experiments of one of us (Hirst, 'J. C. S.', vol. 127, p. 657 (1925), and of White and Tolman ('J. Am. C. S.' vol. 47, p. 1,240 (1925)) proved this to be erroneous. In addition, it has been shown that the reaction proceeds uniformly according to the unimolecular law even in the presence of extensive glass surfaces, or of gases which may be either indifferent, such as argon and nitrogen, or the products of reaction, such as nitrogen tetroxide or dioxide or oxygen.

The rate of reaction may be expressed in the form

$$-\frac{dC}{dt} = 4.98 \times 10^{13} e^{-\frac{24,700*}{RT}} \cdot C.$$

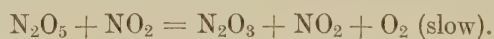
Attempts have been made to interpret the experimental results on the hypothesis that the reaction is in reality bimolecular, and only apparently unimolecular in character; but owing to the abnormally large value of the energy of activation, namely, 24,700 calories per gram. molecule, the number of molecules which could be activated per second by inelastic collision, calculated according to the kinetic theory, falls far short of the observed reaction rate, being, in fact, some 10^5 times smaller.

To overcome this difficulty of the enormous rate of decomposition associated with such a large energy of activation, several alternative hypotheses have been advanced as to the source of this energy of activation, which, as we have noted, cannot be supplied by bimolecular collision alone. With Perrin (*loc. cit.*) we may assume that the decomposition is in reality photochemical, being produced by the inflow of radiation from outside the reaction vessel. That in a black-body enclosure at 25°C. , the rate of inflow of mono-chromatic radiation of frequency determined by the relationship $E = N h \nu$, equivalent to 24,700 calories, falls far short of the amount necessary to give the observed reaction velocity, was first pointed out in a definite manner by Christiansen and Kramers ('Z. Physikal. Chem.', vol. 104, p. 451 (1923)), and thus a reconsideration of Perrin's postulate was necessary. Various attempts have been made to sustain this theory of photochemical decomposition. We may assume that a large fraction, if not all, of the inflowing radiation is available for activation by postulating absorption of a continuous range of frequencies (*cf.* Tolman, 'J. Am. C. S.', vol. 42, p. 2,506 (1920); *ibid.*, vol. 47, p. 1,524 (1925); and Rideal, 'Phil. Mag.', vol. 42, p. 158 (1921)), corresponding to lines in the complete absorption spectrum of the reactant. This view may be further

* The mean value obtained from the data of Daniels and Johnston and Hirst.

modified by the assumption that the light quanta are discrete, of relatively large cross-section, thus facilitating collision and subsequent absorption (see Rideal, 'Phil. Mag.', vol. 40, p. 463 (1920), and Lewis and Smith, 'J. Am. C. S.', vol. 47, p. 1,508 (1925)). This elaboration, however, still awaits more precise formulation, especially with respect to the temperature co-efficient of the reaction and the energy available for activation. We may note that no justification can be found for decreasing the energy of activation by the assumption of Lewis and Smith (*loc. cit.*, p. 1,512) that the critical energy increment is the amount of internal energy required to activate a molecule containing no internal energy at all, for by definition the critical energy increment is the amount of energy required to activate a molecule possessing the *average* amount of internal energy corresponding to the particular temperature in question. In addition, the total radiation inflow does not increase exponentially with the temperature as is the case of the chemical reaction under consideration.

The alternative explanation consists in a chain mechanism of some kind. Perrin first suggested that a quantum of mono-chromatic radiation might be re-ejected after it had been absorbed by a molecule which it excited, and subsequently pass on to another, thus forming a quantum chain. On this view one quantum would have to activate some 4×10^6 molecules before it became degraded, and this number of molecules activated by one quantum would appear to be independent of the pressure of the gas over wide ranges. Christiansen and Kramers ('Z. Physikal. Chem.', vol. 104, p. 451 (1923)), rejecting the radiation hypothesis, have advanced a molecular chain mechanism, in which they imagine that two reactions take place, in the following sequence :



The molecule designated as $\underline{\text{NO}_2}$ is to be regarded as a tautomeric form of nitrogen dioxide, possessing internal energy of activation. On this view, we must imagine the chains as starting by bimolecular collision between nitrogen pentoxide molecules and following the above sequence until an active $\underline{\text{NO}_2}$ molecule loses its internal energy and reverts to the normal form. With a concentration of nitrogen pentoxide of 1.5×10^{-2} mols. per litre, the chains would have to include some 5×10^3 molecules before coming to an end. The most cogent argument against this hypothesis arises out of the investigations on the action of both ozone and oxygen on the reaction velocity. Apparently, according to Hirst (*loc cit.*) and White and Tolman (*loc. cit.*), the reaction proceeds at its normal speed even in the presence of these gases. Whilst nitric oxide is but

slowly oxidised by oxygen (Bodenstein, 'Zeit. f. Elektrochem.,' vol. 24, p. 183 (1918)), it is rapidly affected by ozone, and thus the hypothesis of N_2O_3 being link in the chain is highly improbable.

It seemed of interest to examine the rate of decomposition of nitrogen pentoxide at pressures so low that either the quantum chain of Perrin or the molecular chain of Christiansen and Kramers would be so long that impact of a quantum or an active molecule on the walls of the vessel during the course of a chain would occur. A decrease in the reaction velocity would then be expected. Whilst this work was in progress Hunt and Daniels ('J. Am. C. S.,' vol. 47, p. 1,602 (1925)) have published a series of data on the decomposition rate of the gas at low partial pressures in presence of nitrogen, in which the usual unimolecular constant was obtained. A few isolated determinations of the rate, in the absence of any diluent, by an admittedly somewhat inaccurate colorimetric method at pressures of 1.1 to 2.1 mm., likewise failed to reveal any divergence from the normal.

By the experimental method adopted in this investigation, it has been found possible to follow in an almost continuous manner the rate of decomposition both in the presence and absence of diluents down to pressures so low that each molecular "chain," if it existed, would be submitted to impact on the walls some forty times, and a quantum chain would suffer some thousand reflections. No retardation in the velocity of decomposition was observed, but, on the contrary, it was found that below a certain critical pressure, not of the nitrogen pentoxide but of the total gaseous constituents in the reaction vessel, viz., ca. 0.25 mm., the reaction velocity constant began to increase, approaching, with decreasing pressure, a value about five times that obtaining at high pressures, the rate of reaction thus approaching under these extremely low pressures the rate anticipated from the equation

$$-\frac{dC}{dt} = ve^{-\frac{Nh\nu}{RT}} C. \text{ or } 2.59 \cdot 10^{14} e^{-\frac{24,700}{RT}} \cdot C$$

originally suggested by Dushman ('J. Am. C. S.,' vol. 43, p. 397 (1921)) and Rideal ('Phil. Mag.,' vol. 40, p. 461 (1920)). This result leads to some interesting conclusions in respect to the mechanism of unimolecular reactions which we hope to return to later.

Experimental Procedure.

The course of the reaction was followed by freezing out in a side-tube the nitrogen pentoxide and tetroxide and measuring the oxygen pressure present at various time intervals (fig. 1). Owing to the corrosive nature of the gas, it was

considered necessary to eliminate as far as possible all contact with tapgrease, and to this end, after various unsuccessful trials of quartz fibre manometers, it

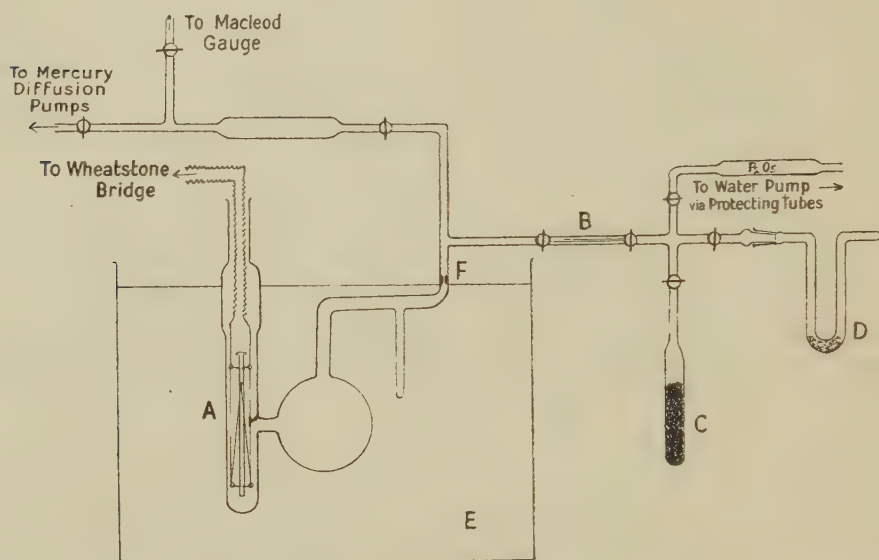


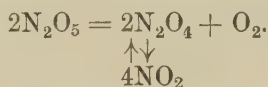
FIG. 1.—A, Pirani-Hale gauge. B, Capillary injector. C, Charcoal. D, Solid nitrogen pentoxide. E, Thermostat. F, Constriction for seal.

was finally decided to measure the oxygen pressure by means of a vacuum gauge of the Pirani-Hale type, the filament and connections of which were constructed entirely of platinum. After the admission of the gases, the reaction vessel could then be sealed off and the decomposition allowed to proceed without the gas being in contact with any grease. The electrical system was similar to that described by Campbell (*Proc. Phys. Soc.*, vol. 33, p. 257, 1921), and the gauge was previously carefully calibrated for oxygen against a Macleod, everything being arranged exactly as in an actual experiment. Owing to a slow change in resistance of the platinum filament, due to a lengthening of the wire owing to heating, this calibration was frequently repeated. In all cases, however, it was found that $V^2 - V_0^2/V_0^2$, where V_0 was the voltmeter reading for the best vacuum obtainable, and V the reading for a given pressure, was practically a linear function of the pressure.

Before every experiment the apparatus was evacuated by mercury diffusion pumps to a pressure less than 10^{-6} mm. of mercury and the reaction chamber was baked out under vacuum to a temperature of over 300°C . The admission of the nitrogen pentoxide was effected by means of a capillary injector, the crystals having first been well evacuated by a liquid air charcoal tube to ensure

as far as possible the absence of nitrogen tetroxide. The method of preparation of the pure crystals was similar to that described by Hirst (*loc. cit.*). The reaction vessel was so constructed that during the actual decomposition the whole could be immersed in a thermostat, while, when a reading was in progress, all but the very small fraction of the total volume, which was cooled to liquid air temperature to freeze out the condensable gases, was in the thermostat. The filament was only heated after the volatile gases had been condensed. That cold platinum has no appreciable catalytic effect on the reaction velocity was demonstrated by carrying out experiments in which three to four times the surface area of platinum exposed by the gauge filament was placed inside the reaction chamber. The effect of the glass surface, if clean and dry, was also shown to be zero, or at least quite negligible, even at low pressures, by means of large variations in the surface area exposed.

Since it has recently been shown (Hunt and Daniels, 'J. Am. C. S.,' vol. 47, p. 1,602 (1925)), that there is almost certainly no formation at high pressures of nitrogen trioxide during the reaction, it was assumed as before, for purposes of calculation, that the reaction occurs according to the equation



The initial pressure of pentoxide admitted was then obtained direct from the final oxygen pressure. Since, however, varying amounts of decomposition took place during the admission of the pure gas, an initial pressure reading was always taken before the experiment was actually begun. In some cases, the oxygen thus admitted was pumped out before sealing off, whilst the pentoxide was condensed by liquid air. No difference was found in the results, however, whether this was done or not. The velocity constants were calculated assuming the oxygen pressure at any time to be always one-half the amount of pentoxide decomposed. The unimolecular constants were obtained by use of the equation

$$k = \frac{2 \cdot 303}{t_2 - t_1} \log \frac{p_a - p_1}{p_a - p_2}.$$

The unit of time was taken as a minute, while the pressure values were simply obtained by multiplying the observed pressures by two, since in the present experiments the actual amounts of oxygen liberated were measured.

Table I contains a complete summary of the experimental results, while in Table II the details of some typical experiments are presented. In Table I the second column represents the initial pressure of nitrogen pentoxide calculated from the final observed pressure of oxygen; column 3 the approximate total

pressure in the system at zero time, estimated from a knowledge of the amount of oxygen due to the decomposition of the pentoxide during admission; column 4 gives the unimolecular velocity constants, the first figure being that at the start of the reaction, and the second the limiting value to which it has decreased after about sixty minutes have elapsed.

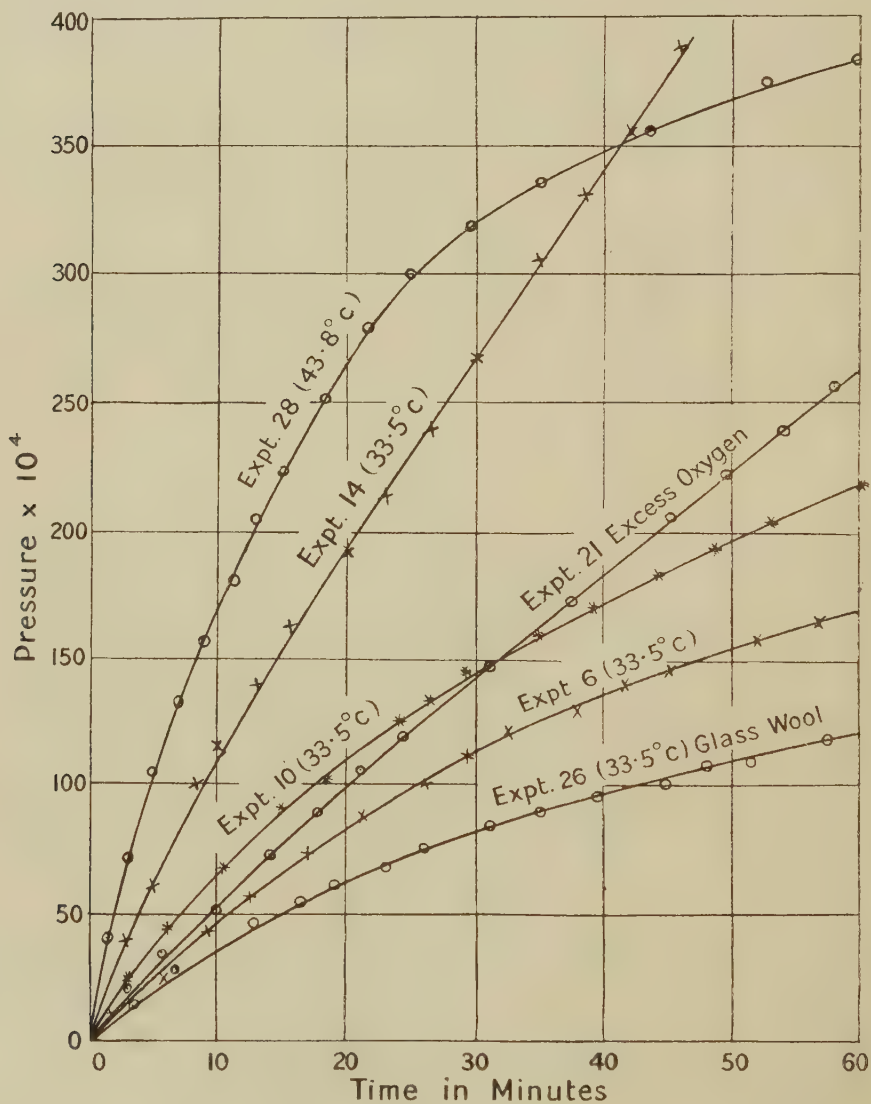


FIG. 2.

Table I.

Expt.	P(N ₂ O ₅).	P (Total).	k (uni) $\times 10^3$.			Remarks.
	Initial	Temperature = 33.5° C.				
3	0.01	0.045	23.5	6.0		
5	0.139	0.180	16.0	11.9		
6	0.056	0.075	17.5	11.0		
10	0.099	0.115	14.7	6.5		
11	0.019	0.050	23.5	9.0		
12	0.143	0.170	12.8	5.9		
13	0.282	0.290	8.65			Small irregular variations in unimolecular constant. Mean value quoted. Extra platinum in bulb. Surface of platinum increased by factor of 3. With Macleod gauge. Ditto. 0.05 mm. O ₂ admitted at start.
14	0.260	0.300	7.89			
15	0.101	0.120	15.4	6.4		
16	0.072	0.095	16.9	8.0		
17	1.280	1.450	6.54			
18	0.035	0.085	21.0	7.3		
19	0.039	0.065	19.4	9.4		
21	0.138	0.220	9.0	7.5		0.028 mm. oxygen present.
22	0.071	0.080	16.8	9.2		
25	0.025	0.035	56.0	11.8		Glass-wool packed bulb. Insufficiently baked out.
26	0.037	0.070	22.9	12.5		Glass-wool thoroughly cleaned and baked out.
		Temperature = 43.8° C.				
28	0.084	0.095	52.0	28.8		
29	0.030	0.065	65.0	36.3		Reaction observed for first 40 minutes only. 0.007 mm. O ₂ present at start.

Some typical velocity curves are shown in fig. 2.

Table II.

Experiment 6 (Temp. = 33.5° C.)	Experiment 12 (Temp. = 33.5° C.)
Initial P N ₂ O ₅ = 0.0556 mm.	Initial P N ₂ O ₅ = 0.143 mm.
Initial P O ₂ = 0.0067 mm.	Initial P O ₂ = 0.0032 mm.

Time (min.).	$p_{O_2} \times 10^4$	k (uni) $\times 10^3$	t .	$p_{O_2} \times 10^4$	k (uni) $\times 10^3$.
0	0	—	0	0	—
10	43	16.9	10	86	12.8
20	83	18.6	20	156	11.8
30	111	15.5	30	215	11.2
40	133	14.1	40	266	10.8
50	152	14.0	50	300	7.9
60	166	11.8	60	324	6.0
Inf.	278	—	Inf.	716	—

Table II—*contd.*

Experiment 14 (Temp. = 33.5° C.)

Initial P N₂O₅ = 0.260 mm.Initial P O₂ = 0.005 mm.

Experiment 19 (Temp. = 33.5° C.)

Initial P N₂O₅ = 0.0386 mm.Initial P O₂ = 0.002 mm.

Time (min.)	$p_{O_2} \times 10^3$	$k \text{ (uni)} \times 10^3$	$t.$	$p_{O_2} \times 10^4$	$k \text{ (uni)} \times 10^3$
0	0	—	0	0	—
10	116	9.33	10	34	19.4
20	192	6.45	20	59	17.1
30	272	7.49	30	77	14.4
40	350	7.88	40	90.5	12.4
50	425	8.22	50	101.5	11.3
60	492	7.94	60	119.0	9.74
Inf.	1300	—	Inf.	193.0	—

Experiment 28 (Temp. = 43.8° C.)

Initial P N₂O₅ = 0.0844 mm.Initial P O₂ = 0.0015 mm.

$t.$	$p_{O_2} \times 10^4$	$k \text{ (uni)} \times 10^3$
0	0	—
10	171	52.0
20	267	48.2
30	321	42.8
40	350	33.8
50	370	32.6
60	383	28.8
Inf.	422	—

Value of k calculated from data of Daniels and Johnston, $k = 25.4 \times 10^{-3}$ at 43.8° C.

Discussion of the Results.

The data obtained point conclusively to the appearance of a disturbance in the rate of reaction when the total pressure in the reacting system falls below 0.26 to 0.28 mm. of mercury. Although the initial total pressure may be below these limits at the start, as the reaction proceeds the pressure increases owing to the decomposition of the nitrogen pentoxide, according to the net reaction $2N_2O_5 = 4NO_2 + O_2$, and as a result the original large value of the unimolecular constant gradually sinks back to the value obtaining at high pressures, viz., $k = 6.35 \times 10^{-3}$.

The observed data have been examined to find out whether the reaction was proceeding according to a bimolecular law at these low pressures, on the hypo-

thesis that two processes, namely, activation and deactivation by collision, were taking place, in which circumstances the reaction velocity would be expressible in the form $-\frac{dC}{dt} = \frac{\alpha C^2}{\beta + \gamma C}$. Whilst some data for particular experiments at 33.5° C. appear to fit the bi-molecular equation more exactly as the initial pressure is lowered, this apparent agreement loses all significance when the experiments at 43.8° C. are considered, in which the variations in the bimolecular constant are found to be very much greater than those of the unimolecular.

Owing to the smallness of the amounts of nitrogen pentoxide admitted, it was evident from the start that the very greatest precautions were necessary. The presence of small traces of dirt would be quite sufficient to ruin an experiment, and in several of the first experiments the gas was found to have decomposed almost completely during its passage through the introducer. Such experiments were always discarded, and are not included in the table of results. In consequence, the lead tubes, by which the introduction of the gas was effected, were thoroughly cleaned with chromic and concentrated nitric acids before each experiment. In the glass-wool experiments, great difficulty was experienced in getting the wool sufficiently dry and clean. However, it will be seen from experiment 26, where the bulb containing the glass-wool had been baked out under vacuum for over six hours at a temperature of 300° C., that the effect of an uncontaminated glass surface is almost entirely negligible.

Again, the experiments in which the surface area of platinum was largely increased rule out the possibility that the observed initial rise in the velocity was due either to a catalytic influence of the filament of the gauge or to some adsorption phenomenon on the filament. The possibility that traces of impurity are the cause of the deviation from the unimolecular law has also been carefully considered, but on this basis it would mean the admission of an amount of impurity unchanging in quantity from experiment to experiment. In view of the fact, however, that widely different pressures of gas were introduced by varied methods, this idea of a constant amount of impurity seems quite untenable. The reaction vessel itself was most carefully cleaned in every case. Thus, after a very careful analysis of the results and of the experimental method, it has been decided that the observed steady decrease in the value of the unimolecular constant must have a real significance, and is not due to any persistent error in technique.

It is clear that this increase in the reaction velocity constant at low pressures negatives the assumption of any type of chain mechanism. If the reaction

velocity constant be plotted as a function of the total pressure of the system, two important observations may be drawn from the curve. It is noted that the unimolecular constant at 33.5°C ., viz., $k = 6.35 \times 10^{-3}$, begins to increase when a critical pressure of some $0.25 - 0.26 \text{ mm.}$ is reached. At this pressure and temperature the mean life of a molecule between collisions is about 4.5×10^{-7} seconds, a value comparable to the mean lives of excited atoms, observed by Wien ('Ann. d. Physik, vol. 60, p. 597 (1919); vol. 66, p. 229 (1921); Dempster ('Phys. Rev.', vol. 15, p. 158 (1920)) and others.

On further decrease of pressure, the reaction velocity constant does not increase indefinitely, but appears to approach a finite value, and by extrapolation it is found that the value obtained at infinitely low pressures should be between $k = 32 \times 10^{-3}$ and $k = 37 \times 10^{-3}$, a closer approximation not being possible on account of the difficulties associated with precise measurements at these extremely low pressures.

These observations are most readily interpreted on the assumption that a definite fraction of the activated molecules always undergo decomposition irrespective of the pressure, but that a larger fraction (approximately four-fifths of the total) of the activated molecules only undergo decomposition if they do not, after activation, suffer collision with other molecules for a period of *circa* 10^{-6} of a second. If collision does take place within this time, deactivation by collision without decomposition must occur. The fraction undergoing decomposition thus increases, as the number of the remaining active molecules which do not suffer collision for about 10^{-6} of a second increases.

The rate of decomposition thus increases as the pressure decreases, until none of the activated molecules are deactivated by collision. According to this view, the rate of decomposition of nitrogen pentoxide for all pressures should be expressed by the equation:—

$$-\frac{dC}{dt} = k_i \left[1 + k_2 e^{\frac{-1.04l \cdot P}{\lambda P_\lambda}} \right] e^{-\frac{24,700}{RT}} \cdot C,$$

where the expression $e^{\frac{-1.04l \cdot P}{\lambda P_\lambda}}$ (*cf.* Jeans, 'Dynamical Theory of Gases,' p. 258) represents the fraction of the active molecules which have a mean free path greater than l at the pressure P . The constant k_1 corresponds to the ordinary unimolecular constant at high pressures, viz., 4.98×10^{13} , with the second as unit of time, whilst k_2 is another specific constant determined by fixing one point only on the pressure—velocity constant curve.

By a series of approximations, it is found that a value of $l = 2.15 \times 10^{-2} \text{ cms.}$, corresponding to a life between collision of 9.5×10^{-7} seconds, when inserted

in the above equation, yields values for the velocity constant in good agreement with the experimental data; the value of k_2 is found to be 4.09, and the equation for the reaction velocity thus reduces to

$$-\frac{dC}{dt} = 4.98 \times 10^{13} [1 + 4.09 e^{-1.003P}] e^{-\frac{24,700}{RT}} \cdot C$$

where P is the total pressure in millimetres and the second as time unit or

$$-\frac{dC}{dt} = 6.35 \times 10^{-3} [1 + 4.09 e^{-1.003P}] C$$

at 33.5°C., with the minute as unit of time.

In fig. 3 the unimolecular velocity constants obtained for the series of experiments during the first five minutes of decomposition are plotted against the total initial pressure, while the values calculated from the above equation are also shown; in fig. 4 the alterations in velocity constant during the progress of

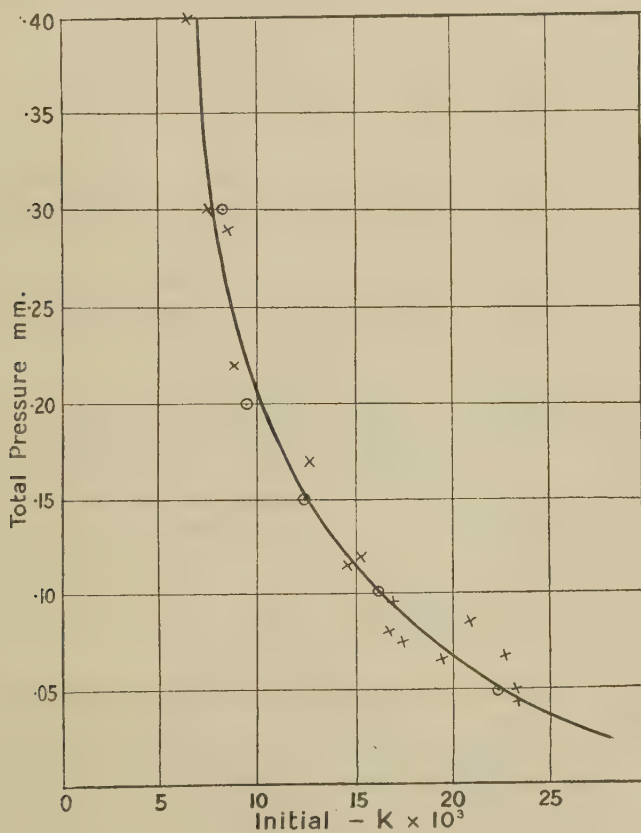


FIG. 3.

decomposition in some typical individual experiments are likewise compared to the calculated values. The same equation also fits quite accurately the experi-

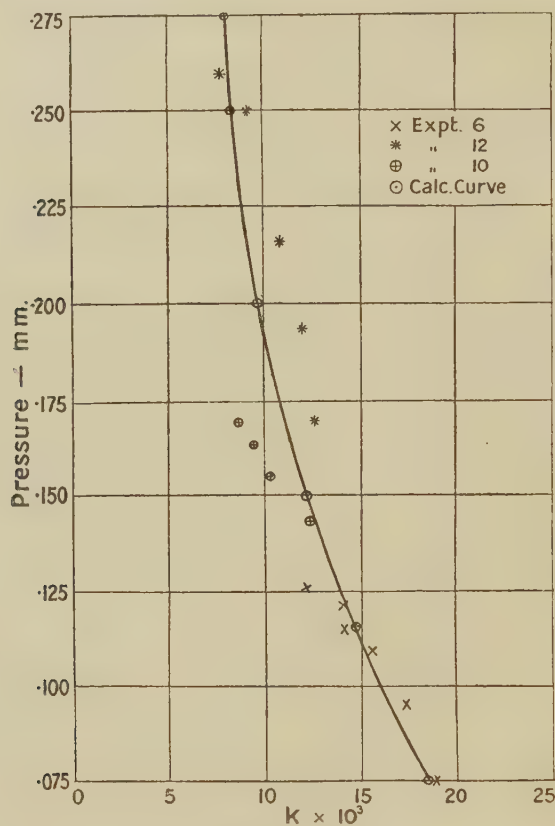


FIG. 4.

mental data obtained at 43.8°C . Thus, at pressures of 0.095 mm. and 0.065 mm. respectively, the observed and calculated velocity constants are

$$55 \times 10^{-3} \text{ observed.} \quad 61 \times 10^{-3} \text{ calculated.}$$

$$65 \times 10^{-3} \quad ,, \quad 72 \times 10^{-3} \quad ,,$$

At very low pressures the equation reduces to

$$-\frac{dC}{dt} = 5.09 k_1 e^{-\frac{24,700}{RT}} \cdot C.$$

Since in absolute units $k_1 = 4.98 \times 10^{13}$ we obtain for the limiting rate of decomposition

$$-\frac{dC}{dt} = 2.53 \times 10^{14} e^{-\frac{24,700}{RT}} \cdot C,$$

or

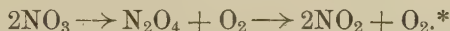
$$\frac{dC}{dt} = 32.3 \times 10^{-3} C,$$

at 33.5°C., with the minute as time unit, a value in agreement with that obtained by extrapolation from the curve. The equation suggested by Dushman and Rideal leads to a reaction velocity of

$$-\frac{dC}{dt} = \frac{Nh\nu}{Nh} e^{-\frac{24,700}{RT}} \cdot C \quad \text{or} \quad 2.59 \times 10^{14} e^{-\frac{24,700}{RT}} \cdot C,$$

a value so close to that determined experimentally that there appears little doubt that the velocity of decomposition of nitrogen pentoxide at extremely low pressures may be expressed by means of this equation.

The reason why only one-fifth of the active molecules decompose on activation, but the remainder have to have an undisturbed life of 9.5×10^{-7} seconds before decomposition will occur, cannot be definitely stated, but the following suggestion is made. In the molecule N_2O_5 there are presumably four NO linkages and one shared NO linkage, and this shared linkage on activation permits of rupture of the molecule into NO_3 and NO_2 , the NO_3 subsequently reacting rapidly in a bimolecular manner according to the equation



If the activation of any one of the five linkages is equally probable, there will on the average be one-fifth active (those of the shared linkage) and 4/5 potentially active molecules present. For the energy of activation to pass from one NO group in the molecule to the one in which rupture can occur, it is necessary that the energy shall pass from one oscillator to another, both, however, being in the same molecule. The time necessary for this passage is naturally identical with the time required for an oscillator to lose or receive its critical energy completely, and is thus of the same order as obtained by Wien and others for the time necessary for an excited atom to lose energy in the form of radiation. If during this period of energy transfer from one part of the molecule to another the molecule suffers collision, deactivation occurs, the energy being presumably dissipated kinetically or by a collision of the second kind.

It may be concluded that the decomposition of nitrogen pentoxide is a true unimolecular reaction, proceeding at a rate given by the equation

$$-\frac{dc}{dt} = \nu e^{-\frac{N\nu_0}{RT}} \cdot C.$$

Since it is clear that the mechanism of reaction cannot involve activation by collision or by the inflowing radiation, and since, in addition, all types of chain

* If every collision between the NO_3 molecules be effective in producing reaction, the velocity of this reaction only becomes comparable with the observed rate of N_2O_5 decomposition at concentrations of ca. 10^{-18} gm. molecules per litre.

reactions are ruled out, we must postulate some type of coupling between molecules undergoing decomposition and those being activated, as first suggested by Polanyi ('Zeit. f. Physik,' vol. 1, p. 337 (1920); vol. 2, p. 90 (1920); vol. 3, p. 31 (1920)). It is hoped to investigate the possibility of arriving at a physical meaning for this hypothetical coupling through the interaction of the molecules with the black-body radiation contained in the system at the given temperature.

Our thanks are due to Sir W. J. Pope, K.B.E., for communicating this paper, to the Board of Scientific and Industrial Research for a research grant to one of us (H. S. H.), and to Messrs. Brunner, Mond and Co. for a grant by which the cost of the apparatus was defrayed.

The Number of Particles in the Beta-Ray Spectra of Radium B and Radium C.

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1. *Introduction.*

The method of analysing a beam of beta-particles by deflecting them with a magnetic field in a vacuum has long been known. The beta-rays of Radium B + C, examined by this magnetic focussing method give a "continuous spectrum" of beta-particles over a wide range of velocities,* on which are superposed lines which are ascribed to the conversion of gamma-rays into beta-rays in escaping from the radioactive atom. There has been considerable difference of opinion as to the origin of the continuous spectrum, whether it consists of the electrons ejected from the nucleus in its disintegration,† or whether it is merely secondary in origin. For example, Pohlmeier,‡ after some experimental work, recently came to the conclusion that the continuous spectrum of Thorium B + C might be due merely to lack of resolution

* Chadwick, 'Ver. Deutsch. Phys. Ges.,' vol. 16, p. 383 (1914); Chadwick and Ellis, 'Proc. Camb. Phil. Soc.,' vol. 21, p. 274 (1922).

† Ellis, 'Proc. Camb. Phil. Soc.,' vol. 21, p. 121 (1922).

‡ 'Zeit. f. Phys.,' vol. 28, p. 216 (1924).

of the line spectrum. He argued that this was probably true also of the spectrum of Radium B + C, a view previously maintained by Meither.*

The relative velocity-distribution of the particles from Radium B + C was examined by Chadwick,† using an electrical counter, and by Chadwick and Ellis,‡ using an ionisation-chamber. In the latter case it is necessary to know the law of the variation of ionising power with velocity of the particles, as well as to estimate the reflection from the walls of the ionisation-chamber; it is difficult to determine these quantities with accuracy. In the measurements by W. Wilson‡ the beta-particles were deflected by a magnetic field into a Faraday cylinder, and the rate of accumulation of charge was directly determined. In the course of experiments made in this laboratory last year, Mr. Curtiss showed that this method could be combined with good focussing if a sufficiently sensitive electrometer were used; an account of the work has been given.§

The object of the present experiments was not only to determine the relative velocity-distribution, but also to measure in absolute magnitude the actual number of particles emitted in the various parts of the spectra. Before any reliance could be placed, however, on quantitative results, it was necessary to come to a definite conclusion on the controversy as to the origin of the continuous background. The first half of the experiments were therefore devoted to this problem. There are two ways of throwing light on the question. The first is to study the effect of varying the experimental conditions, and to find whether, under the best conditions, any large reduction in the magnitude of the continuous background can be produced. The other method is to determine the actual number of particles in the spectrum. For if the continuous spectrum contains all the nuclear electrons, it must clearly contain at least one electron for every disintegrating atom. The weaker line spectrum will be superposed on this. A knowledge of the number of particles in the spectrum should therefore enable us to decide between the rival views.

Besides giving the true velocity-distribution, the measurements have yielded some definite data. First, by integrating the energy in the spectrum, it has been possible to determine the rate of liberation of energy, that is, the heating effect of the beta-particles. Secondly, it has been possible to measure the number of particles in the beta-ray lines of Radium B, and hence to estimate

* 'Zeit. f. Phys.,' vol. 11, p. 49 (1922).

† *Loc. cit.*

‡ 'Roy. Soc. Proc.,' A, vol. 85, p. 244 (1911).

§ 'Proc. Camb. Phil. Soc.,' vol. 22, p. 597 (1925).

the probability that a gamma-ray is converted into a beta-ray in escaping from the disintegrating atom.

2. *Method and Apparatus.*

The beam of particles, limited by a slit near the source, as in the photographic method, was focussed on to a second slit. Below this second slit was placed a Faraday cylinder (see fig. 2). By measuring the rate of accumulation of charge in the cylinder the number of electrons passing through the slit per second was obtained. Thus, the total number of beta-particles of any velocity emitted by a source of known strength can be determined, provided that we know the solid angle containing the beam of particles passing through the second slit.

A Compton electrometer was used to measure the rate of accumulation of charge in the Faraday cylinder. It was maintained at a sensitivity of about 3000 divisions per volt. The deflection was found to be not exactly proportional to the voltage applied to the insulated quadrants. The sensitivity was determined frequently while observations were being made, to ensure that it remained constant. All the measurements were reduced to a standard sensitivity of 3000 divisions per volt, and values mentioned in this paper are expressed in this way.

The Faraday cylinder was embedded in sulphur inside a brass case, as in the experiments of Curtiss. A discharge tube was connected to the box, which was evacuated until the fluorescence produced in the tube by a large spark coil faded out; the Gaede pump was then kept running continuously. The connecting leads to the electrometer passed through a block of lead 6 inches thick to protect them from the action of the gamma-rays, and, in addition, on the near side of the lead block were embedded in sulphur. The airtight insulation was of amber. But it was convenient to find that the electrical leak across the insulators was more than compensated by the presence of a small residual effect of the gamma-rays on the electrometer and its connecting leads, so that the system very slowly acquired a negative charge when a source of gamma-rays was placed near or in the apparatus. This effect, which was small, decreased as the source decayed, and was measured at least twice during every series of observations, and subtracted from the electron currents in the usual way for a "natural leak." This effect already contained that due to the ejection of electrons from the Faraday cylinder by the gamma-rays, so the necessity for making a separate correction for the latter was avoided.

The magnetic field was calibrated up to H_p 2300 by using the known values of the five intense radium B beta-ray lines. This calibration was extended up to higher fields by the use of a fluxmeter.

3. Investigation of the Experimental Conditions.

The principal part of the magnetic spectrum was found to be the continuous background, in agreement with previous workers, part of this being undoubtedly due to particles reflected from the walls of the box. It was pointed out in the introduction that quantitative measurements are useless until spurious particles are eliminated, and the genuineness of whatever continuous spectrum remains is assured. A series of experiments were, therefore, carried out to ascertain to what extent particles of secondary origin entered the Faraday cylinder, to eliminate them as far as possible, and to estimate the unavoidable remainder.

The box was divided into four compartments, A, B, C, D, by means of aluminium partitions, fig. 1. Compartment A contained the radioactive source,

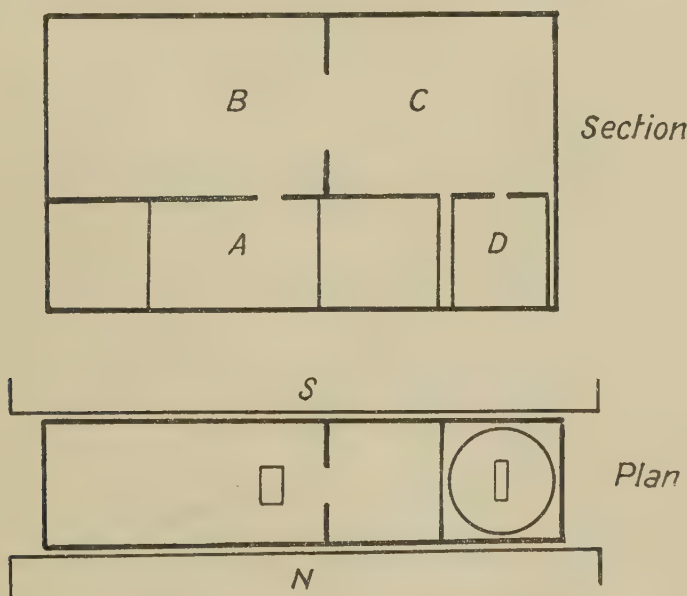
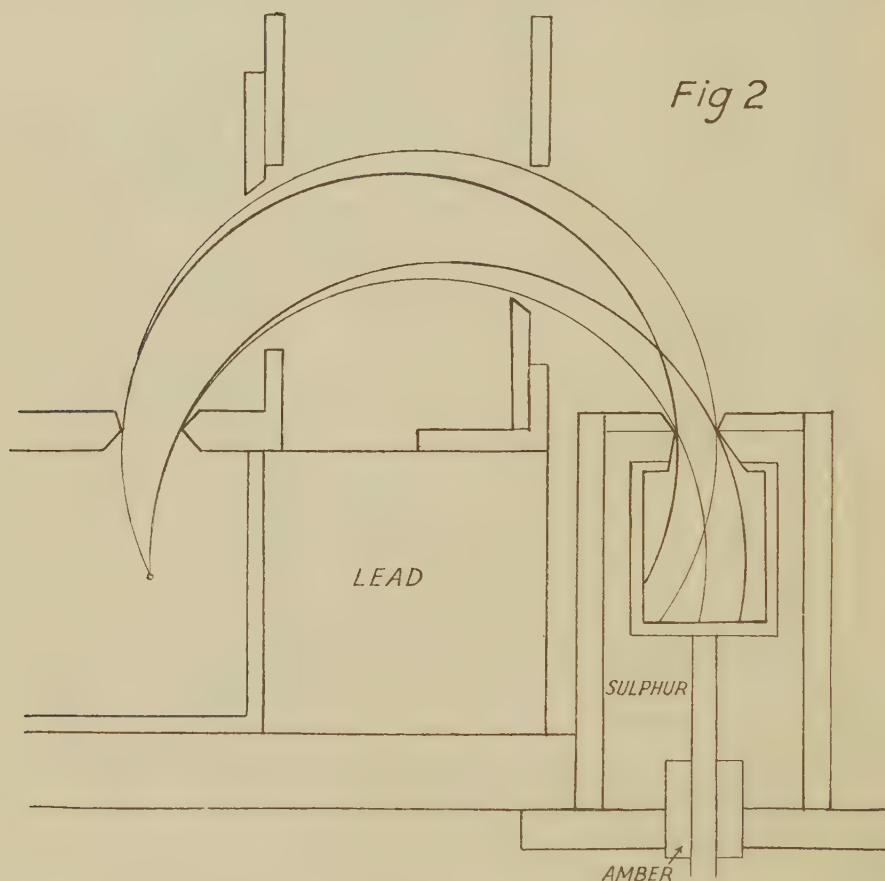


FIG. 1.

of which details are given later, and D contained the Faraday cylinder. The box and the partitions were 3 cm. wide, and the rectangular holes in the partitions through which the particles pass were only 1.1 cm. wide, so that particles reflected from the side walls of the box in A or B could only pass into C in a diagonal direction across the box, thereby missing the slit into D.

It is easier to protect the Faraday cylinder from stray particles than it is to protect the plate in the photographic method. For, when a number of beams of particles of different radii of curvature are being focussed on to the same photographic plate several centimetres in length, the plate is unavoidably exposed to stray particles. But since, in the present method, we are dealing with a single beam focussed on to a small slit, the latter can be better protected. For this purpose a fourth partition (with a rectangular slit 1.2 cm. wide) was added in compartment C, as shown in fig. 2. Measurements made before



and after the insertion of this partition showed that it was effective in cutting out some stray radiation, for the currents were 7 per cent. smaller than those previously obtained.

It is clear, however, that no arrangement of screens could cut out the particles reflected from the surfaces below the source, for these particles mingle with

the direct stream. It was necessary, therefore, to estimate the correction to be applied for this effect. Measurements were accordingly made with the cavity A lined (a) with lead, and (b) with graphite. In the latter case, as was to be expected, the electron current was smaller. At H ρ 2700 the results of two series of measurements gave the ratios of (a) to (b) as 1.09 and 1.08. At H ρ 2200 two comparisons gave the ratios 1.07 and 1.08.

If now N is the number of particles entering the Faraday cylinder direct from the source, if R is the additional fraction entering after reflection at the surface considered, and if S is any additional fraction that may enter after scattering elsewhere, then the current measured is $N(1 + R + S)$. And we have seen that

$$\frac{N(1 + R_{Pb} + S)}{N(1 + R_g + S)} = 1.08.$$

Now Kovarik and McKeehan* found that the number of beta-particles reflected from a surface of graphite was one-quarter of the number reflected by lead. We may, therefore, write $R_{Pb} = 4R_g$, and obtain

$$R_g = 0.020(1 + S).$$

Since S is small compared with unity we find that there is a correction of about 2 per cent. to be subtracted for reflection from the graphite surface.

Next, to ensure that no appreciable part of the current was being contributed by slow particles of secondary origin, the slit above the Faraday cylinder was closed by a piece of aluminium leaf. Measurements were made with the slit open and covered at H ρ 1200 and at H ρ 2800, but no certain difference due to the presence of the foil could be detected. This also ensures that no appreciable number of positive ions formed in the residual air were being drawn into the Faraday cylinder due to its negative charge.

The slit, which limited the beam of particles above the source, was 4 mm. thick, with bevelled edges. These were designed to minimise reflection at the edges; nevertheless, the metal of which they were composed might have some effect on the number of particles. Identical slits of lead and of aluminium were accordingly tried, measurements being made at H ρ 1200 and at H ρ 2450, but no certain difference was observed.

Since the natural leak was measured with the magnetic field reversed, any spurious effect whose magnitude does not depend on the direction of the magnetic field will be eliminated in subtracting the natural leak. This applies to the action of the gamma-rays on the Faraday cylinder itself, as stated

* 'Phys. Zeit.,' vol. 15, p. 434 (1914).

above; but we must consider particles liberated by gamma-rays in other parts of the box, which may pass through the slit into the cylinder. The remarks made at the beginning of this section concerning the reflection of particles from the side-walls of the box apply equally to particles ejected by gamma-rays. Electrons liberated from the walls of the first three compartments can only pass into the next in a diagonal direction across the box, thereby missing the slit into the Faraday cylinder. The compartment immediately above this slit is, therefore, the only important one. According to Compton's theory, not only photoelectric absorption but also scattering will eject electrons. By calculating the solid angle which unit area of surface subtends at the radioactive source, we can obtain the fraction of the gamma-ray energy passing through the surface. Assuming that each gamma-ray absorbed gives rise to one electron, and that all electrons liberated within a depth of 1 mm. below the surface succeed in escaping, we find that the total number that chance to pass through the slit into the Faraday cylinder must be very small. And since this is small, the differential effect on reversing the magnetic field, which is what we require, must be negligible.

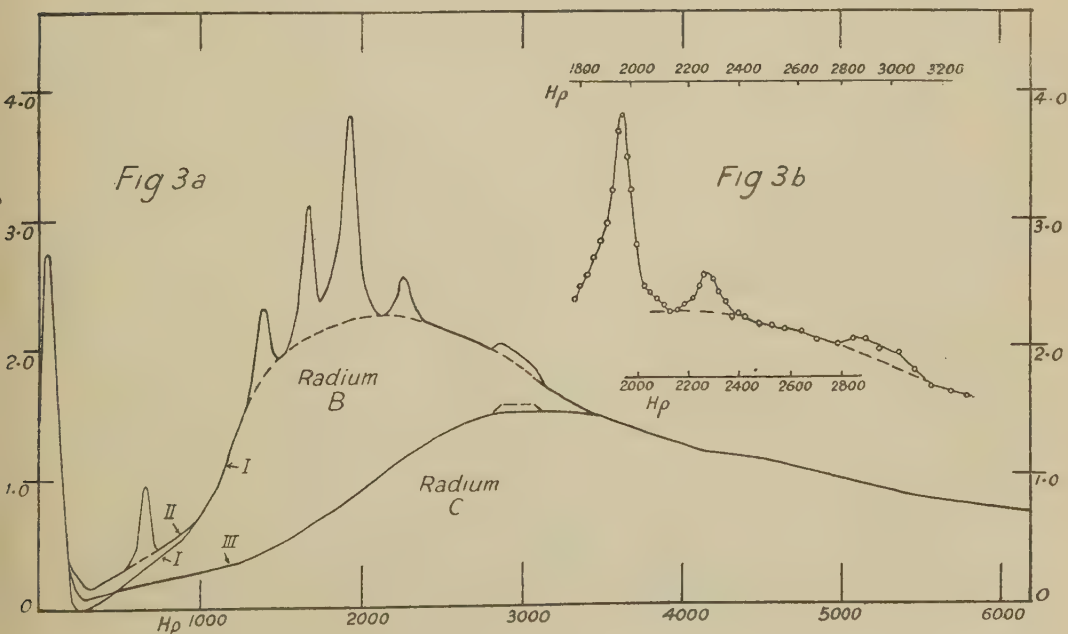
Beta-particles which have entered the Faraday cylinder will be largely reflected from the base of it, and it is necessary to estimate the small fraction that will escape again through the opening. The correction is small, since the solid angle subtended by the slit at a point on the base below is only 0.25, which divided by 2π gives 0.04. Those particles which have lost much of their energy on reflection will be prevented from escaping by the great curvature of their paths in the magnetic field, so that the fraction escaping is difficult to estimate. If we suppose that one-quarter of the particles entering the Faraday cylinder are reflected with sufficient velocity, there will be a correction of one per cent. to be added. This correction has been used in the calculation of the number of particles.

Lastly, we wish to ensure that no electrons enter the Faraday cylinder, except those emitted by the radioactive atoms (having either passed through the slits directly or after the reflections already considered from the material near the source). If there were any range of velocities in which no particles were emitted by the radioactive atoms we could test this. For if there were known to be a gap in the spectrum we could adjust the magnetic field to the intensity appropriate to the $H\rho$ value of the gap, and then no particles ought to be found to enter the Faraday cylinder. This decisive test we can make by using as source an "emanation-tube," a thin-walled glass tube containing Radon; for if the walls of the tube have a thickness equivalent to 2.5 cm. of

air in stopping power for alpha-particles, beta-particles of velocity less than H_p 270 will be unable to penetrate the walls. If, therefore (the radius ρ being 3 cm.), with a field of 80 to 90 gauss, we find that no particles enter the Faraday cylinder we have evidence that we have been successful in eliminating particles of secondary origin, either projected from the walls of the emanation-tube by the fast beta-particles, or else due to reflection of fast beta-particles which will be streaming all the time into compartments B and C. When this test was tried no current was obtained, the slow rate of charge being indistinguishable from the natural "leak" obtained with the field reversed. This is a very satisfactory result, and we may feel confident that whatever continuous spectrum is obtained under these conditions comes from the radioactive atoms themselves.

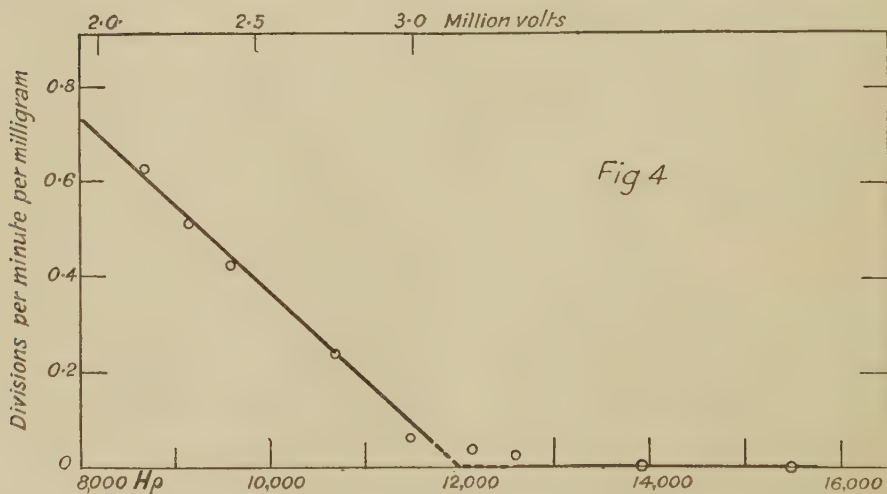
4. *The Magnetic Spectra.*

The curves obtained by plotting the rate of charge against values of H_p are shown in fig. 3. Curve I is for an emanation-tube ; Curve II is for a bare source of active deposit on a plate ; and Curve III for pure Radium C. If radioactive material deposited on a metal plate is used as the source, it is difficult to estimate the true number of beta-particles emitted, owing to the large fraction of particles reflected from the surface of the plate. Most of the measurements were therefore made using "alpha-ray tubes," thin-walled glass



tubes containing Radon. In this case the beta-particles escape from the tube equally in all directions; particles reflected back from the front wall of the tube are compensated by particles reflected forward by the back wall. Thus, though the straggling of the particles in the glass may broaden the beta-ray lines, it will not affect the total number of particles, except the slowest which are unable to penetrate the glass walls. These walls had a stopping power for alpha-particles equivalent to only 2.5 cm. of air. To avoid the need for any correction for absorption the particles of low velocity were examined using bare sources of Radium B + C deposited on a brass plate (Curve II). It might have been thought that the rapid fall in Curve I (fig. 3) between H_p 1300 and H_p 1000 was due to increasing absorption of particles in the glass walls. It was found, however, that the spectrum for a bare source fell equally rapidly here.

Curve I has been used as standard, and Curves II and III have been corrected for reflection by referring them to Curve I. To separate the spectrum of Radium C from that of Radium B, sources of pure Radium C deposited on a nickel plate were used. The currents obtained for Radium C above H_p 3500 were actually greater than those obtained with an emanation-tube, owing to the reflection from the nickel plate; but the spectrum fell towards H_p 12,000 like the spectrum of B + C (fig. 4). The values for Radium C have been everywhere



reduced in Curve III, so that for high velocities they fit the Curve I. The area lying between Curve I and Curve III represents the particles from Radium B alone. The spectra for both B and C are in general agreement with the ioni-

sation measurements of Chadwick and Ellis, though differing in details. They gave the upper limit of the continuous spectrum of Radium B as $H\beta$ 2300. To determine this accurately it would be necessary to find exactly where the two curves I and III join, which is not possible; but since they only claim an accuracy of about 10 per cent. the new value is doubtless more correct.

In fig. 4 the curve for an emanation-tube is plotted for higher velocities; a wider slit* was used than in fig. 3. When the field-strength is increased until the end of the spectrum is approached, a value will be reached at which the fastest particles present fall at the further edge of the slit above the Faraday cylinder. A value will subsequently be reached at which the fastest particles fall short of the slit; but in the interval, which amounts to $840 H\beta$ for the slit used, the curve will tail off, even if the spectrum itself ends sharply. Beyond $H\beta$ 9000 the curve is seen to fall linearly towards $H\beta$ 12,000. Measurements were made up to about $H\beta$ 16,000, but no further rise was found. The limit $H\beta$ 12,000 corresponds to an energy of 3,150,000 electron-volts, and is in agreement with the results of Varder, Chadwick, and some unpublished work of Madgwick done in this laboratory.

The intense beta-ray lines of Radium B, $H\beta$ 1410, 1677, and 1938 appear to be incompletely resolved; this is due to the presence of the lines $H\beta$ 1496, 1774 and 2015, each having an intensity about one-fourth of the main lines, in addition to some fainter lines.† The peak at $H\beta$ 2260 includes the L and M lines, of which $H\beta$ 1938 is the corresponding K line of the same gamma-ray. The most intense line in the Radium C spectrum is known to be $H\beta$ 2980, and this is the only line found on the curve.

From all three kinds of sources used a large peak below $H\beta$ 200 was found, presumably due to the delta-particles liberated from the source by the alpha-particles present. In the emanation-tubes these particles must have been ejected from the outer surface of the glass walls, since they could not have penetrated the walls. The complete gap in curve I between these secondary particles and the continuous spectrum shows that they have no connection with one another. This gap was mentioned in the preceding section, where it was argued that, since secondary particles did not enter the Faraday cylinder in these weak magnetic fields, there was no reason to suppose that the continuous spectrum found in more intense fields could be attributed to them.

The next step in the argument is to show that the continuous spectrum is independent of the line spectrum. The intense lines stand out so clearly as

* See Table II.

† Ellis and Skinner, 'Roy. Soc. Proc.,' A, vol. 105, p. 170 (1924).

peaks that it is impossible to attribute the background everywhere to a merging of the lines. If the large background below the peaks were due merely to lack of resolution of the lines, we should expect a rapid falling off on the high-velocity side of the peaks, which is not found at all. The known line spectrum of Radium B comes to an end at H ρ 2480, a very faint line. Beyond this the next Radium C lines recorded* are :—

Table I.

H ρ .						Intensity.
2550	..	..	..	..	..	1
2720	..	.	..	..	..	2
2480	..	..	..	..	..	1
2890	..	..	..	..	..	1
2980	..	..	..	..	..	30

Now it is clear from fig. 3 that the line 2980, of intensity 30, is weaker than the line 2256; *a fortiori*, the lines of intensity 1 and 2 in the above table must contribute a negligible number of electrons. Hence, if the continuous spectrum were not genuine, we should expect the curve to be much lower at H ρ 2700 than at 2980. Referring to fig. 3, curve I, we see that, instead of there being a large dip in the curve, the intensity is actually greater at H ρ 2700 than at 2980. So the view becomes untenable which attributes the continuous spectra to lack of resolution of the known line spectra.

It was pointed out in the introduction that there is another criterion to test the genuineness of the continuous spectrum—namely, the numerical argument that, if it is formed by the nuclear electrons, it must contain one electron from every disintegrating atom. This test will be made in Section 6, but before proceeding to the calculation of the number of particles it is necessary to determine the solid angle containing the beam of particles.

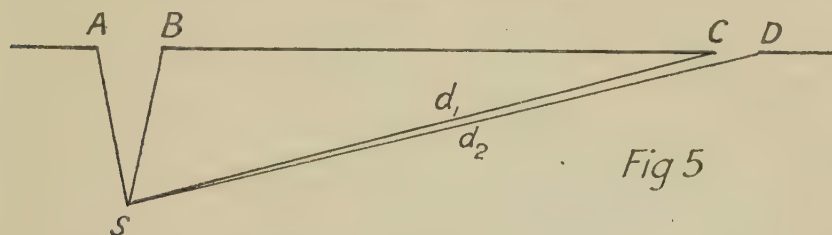
5. The Solid Angle of the Beam of Particles.

Consider a line source below the centre of a rectangular slit of width AB, and of length greater than that of the source. Let the rectangular slit above the Faraday cylinder have a width CD and a length l . Let the distance SC = d_1 , SD = d_2 , and let the angle ASB = 2δ .

The projection of the trajectory on the plane of the paper is a circle. For any value of the field, the beam of particles entering the Faraday cylinder

* Ellis, 'Proc. Camb. Phil. Soc.,' vol. 22, p. 369 (1924).

will consist of particles with velocities lying between two limits. The radius of the smallest circle is given by $\rho_{\min.} = d_1/2$, and of the largest circle by



$\rho_{\max.} = d_2/2 \cos \delta$. We consider tangents to the circles at S, and require to know what directions are permissible if the circle is to pass through AB and CD; and to find the size of the angle ω which includes all permissible tangents at S.

We find

$$\omega_\rho = 2 \cos^{-1} \frac{d_1}{2\rho} \quad \left(\frac{d_1}{2} < \rho < \frac{d_1}{2 \cos \delta} \right), \quad (1.1)$$

$$\omega_\rho = 2\delta \quad \left(\frac{d_1}{2 \cos \delta} < \rho < \frac{d_2}{2} \right), \quad (1.2)$$

$$\omega_\rho = 2 \left(\delta - \cos^{-1} \frac{d_2}{2\rho} \right) \quad \left(\frac{d_2}{2} < \rho < \frac{d_2}{2 \cos \delta} \right). \quad (1.3)$$

We have now to consider the angle which the direction of projection may make with the plane of the paper (fig. 5). This will evidently approximate to $l/2\pi\rho$, since the particle must not have moved a distance from the plane greater than $l/2$ in travelling a length of path $\pi\rho$ on the average. In fact, a consideration of the helical trajectory, too long to be given here, shows that the solid angle sought is given with sufficient accuracy by

$$\Omega_\rho = \frac{l\omega_\rho}{\pi\rho}. \quad (2)$$

This is the solid angle for a particular radius of curvature. To obtain the average solid angle for the beam, which we require, this must be integrated between the limits $\rho_{\min.}$ and $\rho_{\max.}$

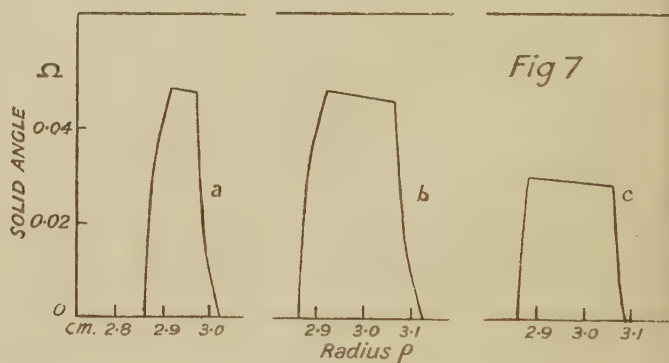
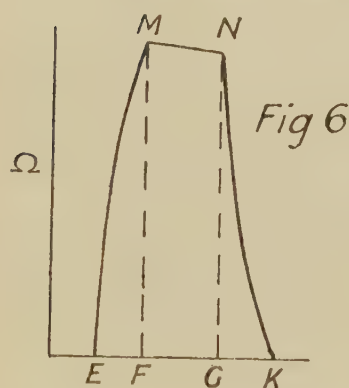
Test of the Solid Angle.—By measuring the electron-currents obtained for any value of $H\rho$ using different combinations of slits, it is possible to test whether their relative values are those predicted from the calculated solid angles. This test will now be described. Three different combinations of slits were used, as shown in the following table :—

Table II.

	Slit AB	Slit CD	Angle δ
	mm.	mm.	°
1	6.0	2.33	10.8
2	6.0	4.22	10.8
3	3.85	4.22	7.08

The values of δ given here refer to the axis of the cylindrical source (emanation-tube); they give with sufficient accuracy the mean value of the angle for different parts of the source. If we calculate values from (1) and (2) and plot Ω against ρ , we obtain a curve with the shape shown in fig. 6. The height FM is determined by the width of the slit above the source, and is independent of the width of the slit above the Faraday cylinder. The length EG, however, is proportional to the width of the latter, and is independent of the slit above the source.

In fig. 7, *a*, *b*, *c*, are drawn to scale the curves for the three combinations of

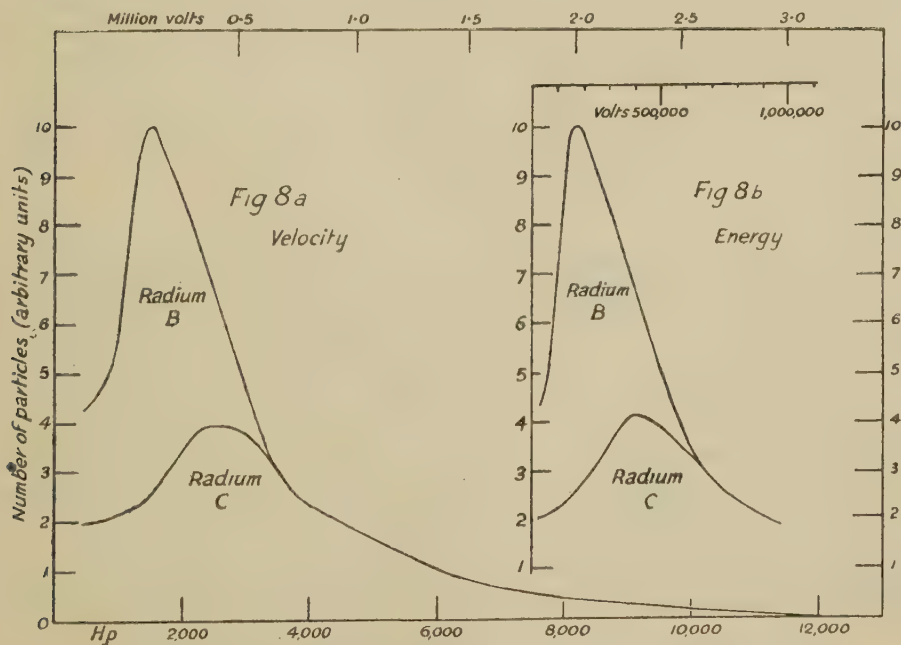


slits given above. The areas under the curves are in the ratio 0.564 : 1.000 : 0.647. The number of particles entering the Faraday cylinder is proportional to the area under the curve, provided that the distribution of the particles is uniform. If the electron-current is measured for each of these combinations of slits, the values should be in the ratio given, provided that the field chosen is one where the curve of the magnetic spectrum is fairly flat. The current obtained at H ρ 2470 reduced to standard sensitivity was 2.13 ± 0.03 divisions per minute for the first combination of slits, and 3.79 ± 0.05 for the second, giving a ratio 0.562 : 1.00. For the second and third pairs the ratio was found to be 1.00 : 0.637, again in good agreement with the calculated values.

6. The Number of Particles.

The experimental curve given in fig. 3 does not at all represent the true velocity-distribution of the particles as emitted by the source. For in a magnetic field of strength H particles are collected over the range $H(\rho_{\max.} - \rho_{\min.})$, and this is proportional to H . For example, in a certain field particles are collected over the range from $H\rho$ 500 to $H\rho$ 530; now, in a field of ten times the intensity, particles are collected, not over the range $H\rho$ 5000 to 5030, but from $H\rho$ 5000 to 5300, that is, over a range ten times as great. Thus in dealing with the continuous spectrum we have to divide the ordinates everywhere by the corresponding field-strength. This has been done in fig. 8, omitting the peaks and following the broken line below the peaks in fig. 3. The shape of the curves is seen to be quite transformed. The continuous spectrum of Radium B, taken alone, follows closely a probability distribution. A probability curve cannot be made to fit the curve for Radium C, but since the latter includes the line-spectrum its exact shape is without significance.

The delta particles have been omitted from fig. 8, for the ordinates would



now become about twenty times as high as the maximum in fig. 8. The number of particles above $H\rho$ 7000 is small; this end of the spectrum would, in fact, not be detected, were it not for the fortunate circumstance that the

sensitivity to small numbers of particles increases in proportion to the field-strength.

The above transformation does not apply to the peaks on the curve, for the relative heights of the peaks above the continuous spectrum are independent of the magnetic field.

The Method of Integrating the Curve.—If the collecting power of the Faraday cylinder were uniform over the range from $\rho_{\min}$ to $\rho_{\max}$, and zero outside this range, the integration to find the total number of particles would be quite straightforward. But since the figures in fig. 6 are not rectangles the process is less simple. The figure must be laid out along the experimental spectrum curve successively, as shown in fig. 9. We wish to make successive curves

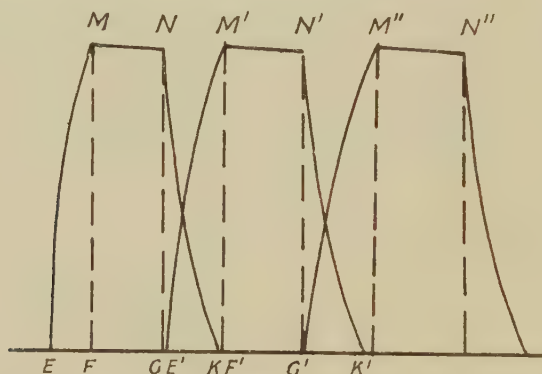


FIG. 9.

overlap so that all velocities are collected to the same extent. The question is where to place E' so that each particle shall be counted in once and only once. We find that E' must be placed exactly at G ; that is to say, that the field-strength must be increased by steps such that $\frac{H'}{H} = \frac{d_2}{d_1}$. Now since $\frac{GK}{EF} = \frac{d_2}{d_1}$ it follows that F' falls at K .

From (1.1) we obtain

$$\omega_{EF'} = 2 \cos^{-1} \frac{H'd_1}{(H'\rho')},$$

and from (1.3)

$$\omega_{GK} = 2 \left(\delta - \cos^{-1} \frac{Hd_2}{(H\rho)} \right).$$

Now, since $H'd_1 = Hd_2$, we obtain by putting $H'\rho' = H\rho$

$$\omega_{EF'} + \omega_{GK} = 2 \left(\delta - \cos^{-1} \frac{d}{\rho} + \cos^{-1} \frac{d}{\rho} \right) = 2\delta.$$

Since in the intermediate portion MN we have also by (1.2) that $\omega = 28$ we find the convenient result that ω is everywhere equal to 28 throughout the whole spectrum. The solid angle is obtained by multiplying by the mean value of $l/\pi\rho$.

The Total Number of Particles. To find the total number of particles between H ρ 500 and H ρ 12,000, the continuous spectrum must be divided into 83 parts. For the value of d_2/d_1 was 1.039, and $\log (1.039) = 83 \log 1.039$. Reading off the values of the current at the 83 places on the experimental curve required, and adding them together, we obtain 90.6 divisions per minute per milligram. To this must be added the current contributed by the peaks; this amount it will be shown is 6.4 divisions per minute. The corrections to be applied are 2 per cent. to be subtracted for reflection at surfaces below the source, and 1 per cent. to be added for loss of particles from the Faraday cylinder. The final value is 96.0 divisions per minute per milligram.

The electrostatic capacity of the measuring system was determined by observing a rate of charge with and without the addition of a Spindler and Hoyer cylindrical condenser of 360 cm. capacity, which had been calibrated at the Engineering Laboratory. The capacity of the Faraday cylinder, electrometer and leads was found to be 87 cm. Thus, a current of one division per minute at the standard sensitivity of 3000 divisions per volt is equivalent to

$$\frac{87}{3000 \cdot 300 \cdot 60 \cdot 4.774 \cdot 10^{-10}} \text{ electrons.}$$

Since the solid angle was 0.0482, the total number of particles emitted in all directions with velocities greater than H ρ 500 is

$$\frac{96.0 \cdot 87 \cdot 4\pi}{3000 \cdot 300 \cdot 60 \cdot 4.774 \cdot 10^{-10} \cdot 0.0482} \\ = 8.45 \cdot 10^7 \text{ electrons per second per milligram.}$$

Since the strength of the source is expressed in terms of equivalent gamma-ray activity, the number of atoms of Radium C* disintegrating per second is that of a milligram of Radium, — $3.72 \cdot 10^7$, according to Hess and Lawson,[†] or $3.40 \cdot 10^7$, according to Geiger's recent determination.[‡] The number of beta-particles emitted is thus found to be either 2.27 or 2.48 from each pair of atoms of radium B and C disintegrating.

* The number of atoms of Radium B in an emanation-tube in transient equilibrium is 0.05 per cent. greater, a correction negligible in this connection.

† 'Phil. Mag.,' vol. 48, p. 200 (1924).

‡ 'Zeit. f. Phys.,' vol. 21, p. 107 (1924).

The calibration of the condenser was said to be accurate to 1 per cent. The measurements of the capacity using the condenser had a mean error of 2 per cent. The gamma-ray activity of the emanation-tubes, compared with the laboratory standard, should not be more than 0.5 per cent. in error. The measurements of the sensitivity of the electrometer should be correct to 1 per cent. The approximations introduced in obtaining the expression for the solid angle should not involve an error of more than 1 per cent. All the measurements necessary to calculate the solid angle should not combine to give an error of more than 1 per cent.

The number of beta-particles found in the spectrum is in agreement with measurements of the total beta-ray emission by previous workers. Danysz and Duane* assumed that the correction to be applied for reflection at the mercury surface below their source was the same as that for brass, whereas it should be much greater for the higher atomic number.† If we double their correction, the final value, which they gave as three electrons, reduces to 2.5 electrons per pair of atoms. Wertenstein‡ used sources of active deposit on aluminium foil. One-half of the beta-particles had to pass through two layers of the foil, together equivalent in stopping power to a centimetre of air. A small number of the slower particles would be absorbed in the foil, so that his value, 2.34 particles per pair of atoms, would be slightly too low. Moseley§ had previously shown that more than 2.2 electrons were emitted per pair of atoms; for he states that his value 2.2 electrons did not include any particles as slow as the lines H ρ 789 and H ρ 661. Thus, we see that these three previous determinations are all in fair agreement with the present measurements.

7. *The Continuous Spectra.*

The evidence is conclusive that the spectrum of Radium B + C contains rather more than two electrons per pair of disintegrating atoms, which strongly suggests that it contains the one nuclear electron from each atom of B and C, with their line spectra superposed. Fortunately, this point can be tested by integrating the number of particles for B and for C separately. We find that the division is nearly equal, each emitting more than one electron, a result

* 'Le Radium,' vol. 9, p. 417 (1912).

† Kovarik and McKeekan, *loc. cit.*

‡ 'C.R. Soc. Sci. de Varsovie,' vol. 9, p. 929 (1916).

§ 'Roy. Soc. Proc.,' A, vol. 87, p. 230 (1912).

in agreement with that of Moseley and of Wertenstein.* Nor is this all, for Radium E is known to possess a continuous spectrum without any line spectrum, and Emeléus† has recently shown that it emits 1.1 ± 0.1 beta-particles. It seems unnecessary to prolong the argument, since the evidence points clearly to the view that in all three cases the continuous‡ spectrum is formed by the disintegration-electrons from the nucleus. Experiments have already been begun with the same apparatus to measure the actual number of particles in the spectrum of Thorium B and C.

8. *The Intensity of the Line Spectrum, and the Internal Conversion Coefficient of the Gamma-Rays.*

By measuring the peaks on the spectrum-curve, we can obtain the actual number of particles in the intense beta-ray lines of Radium B. This determination, though only approximate at present, has some of the characteristics of an absolute measurement.

The absolute height of a beta-ray peak above the continuous spectrum curve will be independent of the width of the slit above the Faraday cylinder, provided that the slit is sufficiently wide to admit the whole line at once. Owing to the broadening of the line due to the passage of the particles through the walls of the emanation-tube, the slit with which the curve in fig. 3 was obtained was not sufficiently wide. In the following table, in column I, are given the heights of the peaks in divisions per minute per milligram, obtained with the wider slit. In the third column these currents are converted into number of electrons emitted per second per milligram, and in the fourth column into number of electrons per hundred disintegrating atoms of either B or C. To avoid speaking of very small fractions, it is convenient to speak of the number per hundred instead of the number per disintegrating atom.

* Though Wertenstein found that Radium B emitted slightly more particles than C, the present results allot slightly more to C than to B. But since the separation depends on correcting for reflection from the source, and this is known to vary with velocity, an exact separation is not possible. Both results, however, agree in allotting more than one electron to each atom of B and of C.

† ‘Proc. Camb. Phil. Soc.,’ vol. 22, p. 400 (1924).

‡ It is, of course, not impossible that the “continuous” spectrum is really a band spectrum. But since the high resolving power obtainable in the photographic method has failed to show any structure, this is improbable. The structure would have to be not only very fine, but also very nicely graded in intensity.

Table III.

Peak.	Divisions per minute per milligram.	Electrons per second per milligram.	Electrons per 100 atoms.	$p\alpha$.
H ρ 661	1.0	$8.9 \cdot 10^5$	2.6	0.026
1410	1.0	8.9	2.6	0.026
1677	1.6	14.4	4.2	0.042
1938	2.2	19.6	5.7	0.057
2256	0.5	4.5	1.3	0.013
2980	0.1	0.9	0.3	0.003

It is unnecessary to repeat here the argument that the beta-ray lines are due to the absorption of gamma-rays not in neighbouring atoms, but almost entirely in the atom in which they originate. The probability that a gamma-ray is converted into a beta-ray, instead of escaping from the atom, has been called the internal conversion coefficient,* and denoted by α by Ellis and Wooster.† If p_1 , p_2 , &c., are the probabilities that the radioactive atom in breaking up emits a gamma-ray of energy $h\nu_1$, or $h\nu_2$, &c., the number of particles in the corresponding lines are $p_1\alpha_1$, $p_2\alpha_2$, &c. In the last column of Table III. values of these quantities are given for the peaks produced by the various gamma-rays.

From these values of $p\alpha$ we may obtain an approximate value for α , by assuming that it is the same for each of the peaks. For the experiments of Kovarik‡ have shown that the average number of gamma-rays emitted by Radium B and C, which is Σp ($1 - \alpha$), is about one per disintegrating atom. Now we see from the above table that the five peaks of Radium B contain 16.4 electrons for every hundred atoms breaking up; or $\Sigma p\alpha = 0.164$. Assuming α to be a constant, we have $\alpha = \frac{\Sigma p\alpha}{\Sigma p} = \frac{0.164}{1.164}$. That is, the probability that a gamma-ray is converted into a beta-ray is nearly 1 in 7.

Since it is uncertain whether the gamma-rays counted by Kovarik included the softest gamma-rays, without including the self-excited X-rays, the above calculation merely gives the order of magnitude. Secondly, our assumption that α has the same value for each of the peaks cannot be true, since the peaks at H ρ 661 and 2256 are due to conversion in the L-levels, and the other three to conversion in the K-level. If we take these three peaks alone we have

* Ellis and Skinner, *loc. cit.*

† 'Phil. Mag.,' vol. 50, p. 521 (1925).

‡ 'Phys. Rev.,' vol. 23, p. 559 (1924).

12·5 electrons for every hundred atoms, yielding a conversion coefficient of 1 in 9, which may be taken as a lower limit. This result is in agreement with the conclusion of Ellis and Skinner,* who estimated that it must be at least 1 in 10. An even greater value has been suggested by Gray† for the gamma-rays of Radium D.

9. *The Heating Effect.*

Having found the true velocity distribution, we may by integrating the energy in the spectrum obtain the heating effect of the beta-particles, a quantity difficult to measure calorimetrically in the presence of alpha and gamma-rays. In the following table is summarised the average distribution of a thousand beta-particles, and of the energy which they carry. In the second column is given the number of particles which lie in the range of velocities specified in the first column. The total energy carried by the particles in each group is given in the third column. The peaks have been included where they occur.

TABLE IV.

				Number.	Energy.
					Volts.
$H\rho$	500	to	1000	94	$4\cdot7\cdot 10^6$
	1000	"	1500	156	20·5
	1500	"	2000	207	46·8
	2000	"	2500	141	47·4
	2500	"	3000	102	46·2
	3000	"	3500	69	39·7
	3500	"	4000	48	34·7
	4000	"	5000	70	63·9
	5000	"	6000	44	52·5
	6000	"	7000	28	41·8
	7000	"	8000	16	28·8
	8000	"	10000	19·4	42·8
	10000	"	12000	5·6	15·3
				Total 1,000	Total $4\cdot85\cdot 10^6$

We see that the average kinetic energy of the beta-particles is $4\cdot85\cdot 10^5$ volts. Now one electron-volt = $1\cdot59\cdot 10^{-12}$ ergs, and $4\cdot18\cdot 10^7$ ergs = 1 gram-

* *Loc. cit.* Both in those and in the present calculations it is tacitly assumed that there is no "white" gamma radiation, the presence of which would make the values of the conversion coefficient higher still. Its presence is unlikely, since Radium E disintegrates without emitting any white radiation, though it too possesses a continuous spectrum of beta-rays.

† 'Nature' (January 3, 1925).

calorie. So that since the number of beta-particles emitted per second is $8.45 \cdot 10^{10}$ per gram, the heating effect is found to be

$$\frac{8.45 \cdot 10^{10} \cdot 4.85 \cdot 10^5 \cdot 3600 \cdot 1.59 \cdot 10^{-12}}{4.18 \cdot 10^7} = 5.6 \text{ calories per hour per gram.}$$

The value obtained by Rutherford and Robinson* by calorimetric measurement was 4.7 calories per hour. But their experiments were concerned chiefly with the heating of alpha-particles, and the beta-ray effect was determined only by the subtraction method.

Analysing the spectrum of Radium B alone in the same way, we find that the average energy of a beta-particle is $2.3 \cdot 10^5$ volts. Hence if equal numbers of particles are emitted by B and by C, the heating effect due to the beta-particles of B alone is found to be

$$1.3 \text{ calories per hour per gram.}$$

The heating effect of the beta-particles of C alone is thus 4.3 calories.

Summary.

The beta-particles from Radium B and Radium C have been examined quantitatively by the method of the magnetic spectrum. The particles were focussed on to a slit, below which was placed a Faraday cylinder, so that the actual number of particles emitted with any velocity could be measured, the solid angle of the beam being known. The effect of varying the experimental conditions was first studied in order to reach a definite conclusion on the controversy as to the genuineness of the "continuous spectrum." The result obtained was that Radium B and Radium C each possess a genuine continuous spectrum. Measurements were then made which yielded the following data.

(1) The continuous spectrum of Radium B rises to a maximum at 170,000 volts, and has an upper limit at about 650,000 volts. The spectrum of Radium C rises to a maximum at about 400,000 volts, and has a definite upper limit at 3,150,000 volts. Curves showing the velocity-distribution are given.

(2) If the continuous spectrum is formed by the electrons ejected from the nucleus we should expect the spectra of Radium B and Radium C (including the beta-ray lines) to contain rather more than one electron for each atom disintegrating. By integrating the number of particles in the spectrum we find that this is the case for both Radium B and Radium C.

(3) By measuring the five peaks on the spectrum-curve the actual number of

* 'Phil. Mag.,' vol. 25, p. 312 (1913).

particles in the beta-ray lines of Radium B are found. From this it is calculated that the probability of a gamma-ray being converted into a beta-ray instead of escaping from the radio-active atom is about 1 in 7.

(4) By integrating the energy carried by the particles in the spectrum, the heating effect for the beta-particles of Radium B + C is found to be 5.6 calories per hour per gram. Of this 1.3 is to be ascribed to Radium B, and 4.3 calories to Radium C.

In conclusion, I wish to express my thanks to Sir Ernest Rutherford for his interest and advice throughout this work, and to Dr. C. D. Ellis for helpful discussion. My thanks are also due to Mr. G. A. R. Crowe for the preparation of the radio-active sources.

On the Velocity of Sound in Mixtures of Gases.

By HAROLD B. DIXON, C.B.E., D.Sc., F.R.S., and GILBERT GREENWOOD, M.Sc.,
late John Harling Fellow of Manchester University.

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In many investigations on the combustion of gases it is desirable to know the specific heat of a *mixture* of gases of which the constituents may vary both as to their heat capacities, and as to the rate of change of these with temperature. For instance, in the determination of the ignition-points of gases and vapours with oxygen or air by the method of adiabatic compression we require to know the mean specific heats of the mixture between the initial and final temperatures; and similarly in the more difficult problem of attempting to calculate the temperatures reached in the explosion of gases we require to know the heat absorbed by the mixed gaseous products. Again, if the explosion wave is propagated by a process analogous to that of a sound-wave, it is important to be sure that the motion of a sound-wave, in a mixture of gases of different densities, can be calculated.

Now very few experiments have been published on the velocity of sound in mixtures of gases—except in the case of nitrogen peroxide, where the dissociating gas mixture is in a state of mobile equilibrium easily altered by slight changes of temperature and pressure. It appeared, therefore, of interest to measure the velocity of sound in a few mixtures of simple gases, and to compare the results

with those derived from Laplace's formula in which the ratio of the specific heats is calculated from the expression :—

$$\gamma = \frac{C_p a + C'_p b}{C_v a + C'_v b},$$

where C_p and C_v are the specific heats of the gas A, at constant pressure and constant volume, and C'_p and C'_v are similarly the specific heats of the gas B, and a and b are the volumes of A and B respectively.

Experimental Procedure.

The method used in the determination of the velocity of sound through the mixtures was the production of stationary waves and "dust figures" in a tube of the gas, Kundt's* double-tube type of apparatus being employed. It consisted of two similar tubes of the same internal diameter, viz., 2.75 cms. Fitted into these tubes by means of thin rubber stoppers was a glass rod of 0.75 cm. diameter, arranged in such a manner that the points where it was held rigid by the stoppers were exactly one-quarter of its total length from its ends. When the central half of the rod outside the tubes was stroked with cotton-wool (wetted with methylated spirits) the rod was caused to vibrate, the two positions where it was held by the stoppers being nodes, and the ends (one in each tube) being points of maximum vibration. To these ends of the rod were glued thin discs of cork, about 0.3 cm. thick, and of such a diameter as to nearly fill the tubes. Passing through a similar stopper at the other end of each tube was a thermometer, with its bulb inside the tube, and to the tip of each was fastened a similar disc of cork. These thermometers served the dual purpose of registering the temperature of the gas within the tubes, and of providing a means of adjusting the length of path of the sound-wave so that it was reflected back along itself. One of the tubes served as a standard and contained dry air, whilst the other tube contained the experimental gas or gas mixture. Along the bottom of each tube was first put a line of lycopodium or other suitable powder. It was found important that the tubes, the gases and the powder should be very dry. Through each rubber stopper passed a glass tube fitted with a tap to make an inlet and outlet to each experimental tube. The first tube was filled by sending a current of dried air through it for a quarter of an hour. The other tube, connected to a pump, a pressure gauge and the gas-holder, was first evacuated; it was then cut off from the pump and filled up to atmospheric

* 'Pogg. Ann.,' vol. 135, pp. 337 and 527 (1868).

pressure with the gas from the gas-holder. This process was repeated three times.

The method of obtaining the dust figures in a convenient form and of measuring them was that used by Partington and Cant.* The tubes were held firmly by clamps at a convenient height above the bench, on which was fastened a metre scale parallel to the tubes. The measuring instrument consisted of a solid base with a pointer moving along the scale; it held two vertical uprights carrying two horizontal threads one above and one below the tube. By moving the instrument until the two threads and the striation to be measured were coincident, the reading of the pointer gave the position free from parallax. Each experimental tube was surrounded by an outer concentric tube which served as a water-jacket and kept the temperature of the gases more constant. The details of a complete experiment are shown in Table I (p. 565). Fresh lycopodium powder, or sometimes ignited sieved silica, was used in each experiment.

The ratio of the two measured wave-lengths λ_1/λ_2 is equal to the ratio of the two velocities in the tubes v_1/v_2 , and since the viscosity correction is very small owing to the large diameter of the tubes, we introduce only a very small error if we put the observed ratio equal to the ratio of the velocities in free gas V_1/V_2 . Hence we get $\lambda_1/\lambda_2 = V_1/V_2$, and, assuming a known value for V_2 (the velocity of sound in free air), we can calculate V , the velocity in the free mixture.

All the velocities were reduced to a common temperature, viz., 20° C., they are therefore all comparable. During the course of the experiments different tubes and rods were used. The two tubes were always compared with each other by carrying out experiments with air in each tube: the mean $\frac{1}{2}\lambda$ for each tube was found and a temperature correction applied when necessary. If there was a difference in the half wave-length value given by the two tubes a "tube correction" was applied to results obtained with gas mixtures in the tube concerned.

Preparation of Gases and Gas Mixtures.

Hydrogen and Oxygen.—These gases were prepared by the electrolysis of a solution of baryta. Electrodes consisting of a stout platinum wire carrying a piece of platinum foil were fused into each limb of a U-tube. A hot saturated solution of twice recrystallised barium hydroxide was poured into the tube; on cooling crystals were deposited. During the electrolysis the solution was

* 'Phil. Mag.,' vol. 43, p. 369 (1922).

heated : this has the effect of dissolving more baryta and increasing the conductivity, and also tends to prevent the formation of ozone. The oxygen was led off from one limb of the U-tube, and the hydrogen from the other, and collected over water in gas-holders.

Owing to the difficulty of making a gas mixture of predetermined composition, mixtures were made up approximately and the exact composition subsequently determined by analysis. The gases passed through drying and purifying trains on their way to the experimental tube. The reagents used for oxygen and mixtures of this with hydrogen were concentrated sulphuric acid, soda-lime and two tubes of solid caustic potash. The sample of gas for analysis was also passed through the drying-trains. The oxygen contained no traces of hydrogen ; a sample was completely absorbed by alkaline pyrogallol ; no difference in the velocity of sound was observed if the gas was first passed over heated copper oxide.

Ammonia.—This gas was obtained from liquid ammonia. A sample was completely absorbed by a sulphuric-acid solution. It was passed through a tube of saturated ammonia solution, as an indicator of the speed of passage. The drying-trains consisted of soda-lime and solid caustic potash.

Nitrogen.—The source of supply was a cylinder of the compressed gas, made from liquid air. By this method of manufacture it is possible to obtain a very pure nitrogen, whilst the oxygen so made is not so pure. The slight amount of oxygen present was removed by the passage of the gas through a tube of alkaline pyrogallol. It then passed through a tube of sulphuric acid and drying-trains filled with soda-lime and solid potash.

Carbon Monoxide.—This gas was prepared by the interaction of sodium formate and concentrated sulphuric acid. The acid was slowly dropped on to the sodium formate in a flask which was warmed. The issuing gas was passed through two towers of concentrated potash solution to remove any carbon dioxide which might be present. It then passed through lime water, which was not turned milky, and was finally collected over water in a gas-holder. A sample of the gas was completely absorbed by ammoniacal cuprous-chloride solution. The reagents in the drying trains between the gas-holder and the experimental tube were alkaline pyrogallol, concentrated sulphuric acid, solid calcium chloride.

Mixtures of nitrogen and carbon monoxide were made up approximately in a mercury gas holder. The gas mixture, on its way to the experimental tube, passed through the drying-trains described above. The composition of the mixture was determined by analysis.

Carbon Dioxide.—This gas was obtained from the impure gas contained in steel cylinders. The main impurity is air dissolved in the liquid carbon dioxide. The crude gas was passed into an evacuated vessel immersed in liquid air, when the carbon dioxide at once froze to a white solid and the uncondensed air filled the condensation vessel, pressure gauge, and the connecting tubes. It was then pumped off, the system being finally evacuated by the mercury pump. The liquid air was removed and the condensation vessel connected to a gas-holder containing mercury. The solid began to vaporise—the first fraction passed through the gas-holder to the air, thus sweeping out any traces of air in the top of the gas-holder. The gas thus prepared was completely absorbed by caustic potash. On its way to the experimental tube the gas passed through drying-trains filled with concentrated sulphuric acid and solid calcium chloride.

Mixtures of Hydrogen and Carbon Dioxide.—These mixtures again were made up approximately in a mercury gas-holder, and the exact composition determined by analysis. The only reagent in the drying-trains was solid calcium chloride.

Experimental Results.

Case I.—Mixtures with γ practically constant, but with varying density. A mixture of this type is obtained by nixing the two permanent gases, hydrogen and oxygen. The results of the experiments are shown in the tables. Table I gives the details of one experiment made with a mixture containing 56.4 per cent. of hydrogen :—

Table I.

Air Tube. Temp. = 15.5° C.				Mixture Tube. Temp. = 16.5° C.	
Figures.	$\frac{1}{2} \lambda$	Figures.	$\frac{1}{2} \lambda$	Figures.	$\frac{1}{2} \lambda$
	cms.		cms.		cms.
1-11	3.413	1-8	3.397	1-6	4.680
1-10	3.393	2-9	3.393	1-5	4.712
2-11	3.416	3-10	3.392	2-6	4.696
1-9	3.394	4-11	3.423	1-4	4.682
2-10	3.393	3-9	3.393	2-5	4.718
3-11	3.417	4-8	3.400	3-6	4.713
—	—	5-7	3.405	3-4	4.725
Mean $\frac{1}{2} \lambda = 3.402$.				Mean $\frac{1}{2} \lambda = 4.703$.	

Using these values to calculate the velocity of sound through the gas mixture, and correcting to 20° C., we obtain the value 474.3 m.p.s. A number of such experiments were made with each mixture, and the final average results are

given in column 2 of Table II. The composition of the mixture is shown in column 1, whilst in the third column is the value of the "tube correction." The final result is given in column 4.

Table II.

Comp. of Mixture. Percentage of H ₂ .	Experimental Result.	Tube Correction.	Corrected Velocity.	Calculated Velocity.
56.4	474.25	—	474.25	475.4
51.6	453.5	—	453.5	454.1
50.2	448.4	—	448.4	448.5
21.0	365.5	— 0.2 per cent.	364.7	364.2
0	328.5	—	328.5	—

The last column shows the calculated velocity of the particular mixture. The density of the mixture was obtained from its known composition and the densities of hydrogen and oxygen as determined by Morley,* who found 0.0000899 gm. as the weight of 1 c.c. of hydrogen at 0° C. and atmospheric pressure, and 0.001429 as the corresponding figure for oxygen. The γ 's for the mixtures were calculated from the formula using the following values of the specific heats, as determined by Scheel and Heuse†:—

$$\text{Hydrogen} \dots C_p = 6.860 : C_v = 4.875.$$

$$\text{Oxygen}^\ddagger \dots C_p = 6.982 : C_v = 4.989.$$

The agreement is good. The results are shown graphically in fig. 1, in which the experimental points are represented by $\times$ and the calculated by O. As the mixture becomes lighter, *i.e.*, richer in hydrogen, the difficulty in obtaining good dust-figures increases. With mixtures containing 70 per cent. or more hydrogen, it was indeed found impossible to obtain dust-figures at all. Difficulties of this nature have been mentioned by Travers§ in connection with helium and neon. The graph in this region is constructed from calculated values, the values for an 80 per cent. mixture and for pure hydrogen being 652.6 m.p.s. and 1305 m.p.s. respectively.

* 'Zeit. Phys. Chem.,' vol. 20, p. 242 (1896).

† 'Ann. Phys.,' vol. 40, p. 473 (1913).

‡ A series of direct measurements in a long pipe gave the velocity of sound calculated for "free oxygen" at 20° as 326.8 metres per second; this value gives $C_p - C_v = 1.9947$, and $C_p/C_v = 1.403$. But, as we could not secure satisfactory measurements of the velocity of sound in hydrogen in a long tube, we have taken the values given above.

§ 'Study of Gases,' 1901 edition, p. 274.

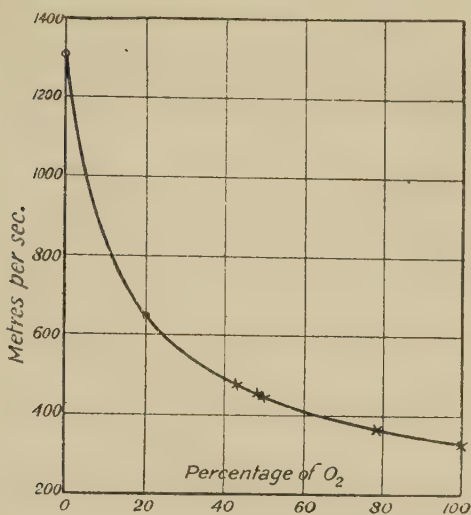


FIG. 1.

Case II.—Mixtures with both the density and γ variable.

Carbon dioxide and hydrogen provided mixtures of this type. The mean results obtained are given in Table III.

Table III.

Comp. of Mixture. Percentage of CO ₂ .	Experimental Result.	Tube Correction.	Corrected Velocity.	Calculated Velocity.
100	269.1	Per Cent. —0.4	268.0	—
65.9	327.2	+0.4	328.5	329.8
49.5	378.2	—	378.2	379.0
38.8	423.1	+0.4	424.8	424.8

In the calculation of the velocities in the last column, the following values were used :— C_p and C_v for carbon dioxide 8.797 and 6.746 respectively as found by Dixon*; Scheel and Heuse's values for hydrogen, and Rayleigh's† density of CO₂, *i.e.*, 1.9651 gm. per litre at N.T.P.

These results are given in the graph of fig. 2, where calculated points are represented again by O and experimental points by ×.

* 'Proc. Roy. Soc.,' A, vol. 100, p. 1 (1921); A, vol. 105, p. 200 (1924).

† 'Proc. Roy. Soc.,' A, vol. 62, p. 204 (1897).

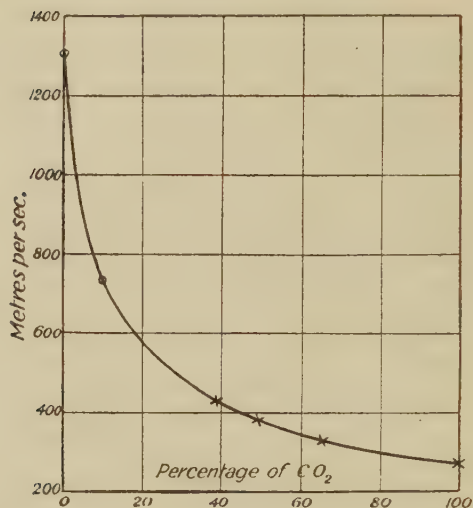


FIG. 2.

Case III.—A more complicated mixture. This was supplied by a mixture of carbon dioxide, hydrogen and air. The result is given in the next table:—

Table IV.

Composition of Mixture.	Experimental Result.	Tube Correction.	Corrected Velocity.	Calculated Velocity.
CO ₂ =43·5 per cent H ₂ =51·2 per cent Air=5·3 per cent.	387·7	0·4 per cent.	389·2	389·3

The value obtained for the calculated velocity of sound in the mixture at 20° is 389·3 m.p.s. The agreement is satisfactory.

Case IV.—Mixtures possessing a constant γ and a constant density. Mixtures satisfying these conditions were made with carbon monoxide and nitrogen. The results obtained are given in Table V and fig. 3.

Table V.

Comp. of Mixture. Percentage of N ₂ .	Experimental Result.	Tube Correction.	Corrected Velocity.
100	351·2	—	351·2
83·8	351·8	—	351·1
52·8	352·4	—0·2 per cent.	351·7
39·4	351·6	—	351·6
0	351·8	—	351·8

Since the ratios of the specific heats and densities of carbon monoxide and nitrogen are practically identical, there should be no change in the velocity of sound on varying the composition of the mixture. Fig. 3 shows that this is the case.

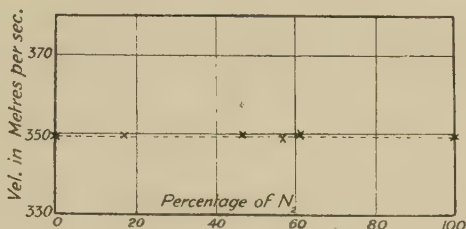


FIG. 3.

Case V.—Comparison of a single gas with a gas mixture of the same density. The single gas chosen was ammonia and the gas mixture equal volumes of hydrogen and oxygen. The velocity of sound as determined in ammonia is given in Table VI. It was found that lycopodium powder could not be used since it was attacked by ammonia. Precipitated silica, which had been strongly ignited and sieved through a fine mesh, was used. It was noticed that ammonia was strongly absorbed by the glass tubes and by the silica. Now, if the velocity of sound in ammonia is multiplied by the square root of the ratios of the γ 's for hydrogen-oxygen mixture and ammonia, we should obtain a calculated value of 446.8 m.p.s. for the velocity of sound in the mixture. But there is a small difference between the density of ammonia and that of a mixture of equal volumes of hydrogen and oxygen; allowing for this, the calculated velocity in the mixture becomes 447.1 m.p.s. The result is shown in Table VI.

Table VI.

Experimental Velocity in NH ₃ .	Tube Correction.	Corrected Velocity in NH ₃ .	Calculated Velocity in Mixture.
433.9 m.p.s.	— 0.2 per cent.	433.0	447.1

The value given by the curve through our experimental numbers is 448.0 m.p.s., for the mixture of equal volumes of hydrogen and oxygen.

Magneto-Striction in Iron Crystals.

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§ 1. *Introduction.*

The phenomenon of magneto-striction, or change in dimensions of a body when magnetised, has been known for a long time. It was discovered by Joule in 1847, and has since been the subject of many careful investigations. The phenomenon has been measured in many kinds of iron, nickel, and cobalt. The results have shown that the exact nature of the phenomenon depends to a great extent on the physical state of the specimen examined, and may be considerably altered by physical treatment, such as annealing. This result follows from the known effect of crystalline structure on the properties of ferro-magnetic substances. It is to be expected that the results, and their interpretation, would be considerably simplified if found in single crystals. In this case, instead of there being indeterminate heterogeneous crystalline mass, the specimen would have a definite crystal lattice with reference to which the axes of the specimen could be determined. This has been pointed out by various writers, and some work has been done in this direction.

Heaps ('Phys. Rev.', vol. 22, p. 486, 1923; vol. 23, p. 60, 1924) has investigated the magneto-striction of single crystals of iron and magnetite. The experiments on iron were carried out on a disc cut from a single crystal. The elongation parallel to the magnetizing field was measured for various directions in the disc, and it was found that the elongation varied considerably with the direction. The direction of the crystal axes were not determined, and the interpretation of the results is, therefore, difficult. Moreover, the crystal contained about $3\frac{1}{2}$ per cent. of silicon. These experiments are also open to the objection that, with specimens of the shape used, it is difficult to obtain uniform magnetization except with very strong magnetic fields. The experiments on magnetite were more complete. A single crystal approximately spherical in form was used, and the position of the crystal axes known. In this case, the elongation was found to vary in a regular way with reference to the crystal axes. In neither of these experiments, however, was the intensity of magnetization measured. It may be mentioned that the intensity of

magnetization is probably an important factor in the phenomenon of magnetostriction, as this phenomenon seems to be intimately connected with the orientation of the atoms in the magnetic field.

There were available to the writer some large crystals of iron, several of which had been used in an investigation of the molecular field in iron crystals ('Roy. Soc. Proc.,' A, vol. 107, p. 496, 1925). For these crystals the total impurities amounted to only about $\frac{1}{2}$ per cent., and the crystal axes were known, having been determined by X-rays. From these, rods about 1.8 cms. long and 1.2 mms. in diameter were cut parallel to the (1, 0, 0), (1, 1, 0) and (1, 1, 1) directions of the crystals. The change in length of these rods when magnetized longitudinally was measured, the intensity of magnetization and the strength of the magnetic field being determined simultaneously.

It was found that the magneto-strictive effect was quite different in the three directions for which it was measured. For the (1, 0, 0) axis magnetostriction was found to give rise to an increase in length for all values of the magnetization; for the (1, 1, 1) axis there was always a decrease in length; and for the (1, 1, 0) axis an increase in length occurred for weak fields, but was followed by a decrease in length when magnetic saturation was approached. A rod of soft iron gave an effect quite similar to that obtained for the case of a single crystal for the (1, 1, 0) direction. It seemed possible by a suitable combination of the effects obtained for single crystals to explain the general character of the results for soft iron.

§ 2. *Apparatus.*

The apparatus used is shown in fig. 1. The measurement of the change of length of the iron rod requires the use of some device giving high magnification. That used in this research has been frequently used in this type of experiment. It consists of a combination of mechanical and optical levers. The lever was constructed from light glass rods on a cantilever principle, so that it was quite light but rigid. At one end, a thin glass plate was attached with shellac. The glass plate rested on a pointed brass rod, which was soldered to the iron rod. This end of the lever also bore against a fixed brass knife-edge, about $\frac{1}{2}$ -cm. from the pointed rod. It was impossible to use a steel edge in this position as it was too close to the magnetometer. The brass knife-edge was carefully prepared, and seemed to be quite satisfactory. At the other end of the lever, which was about 17 cms. long, there was a light tilting mirror. This mirror was attached to a small table provided with two knife-edges, about 3 mms. apart, made from a razor blade. One of these edges rested on the end of the

lever, and the other on two fixed glass rods parallel to the lever. It was important to make the mirror and table as light as possible, to reduce the disturbing

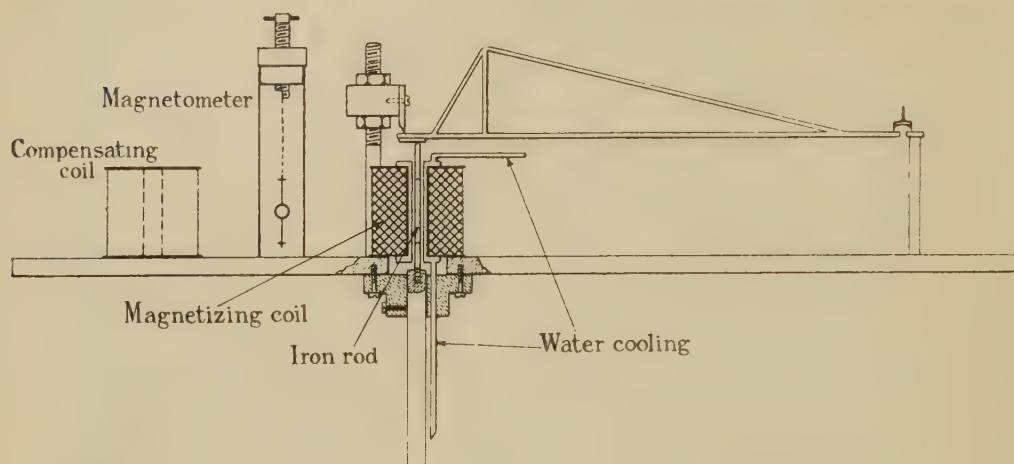


FIG. 1.

effect of vibrations due to inertia and to prevent any lag in the magnifying system due to friction. A small plane galvanometer mirror was used. Through it, by means of a fixed telescope, a millimetre scale at a distance of about 3 metres was viewed. The magnification obtained was about 5×10^4 . Apparent scale motions of $1/10$ mm. could be estimated, so that changes in length of 2×10^{-7} cms. could be detected.

The iron rod was magnetized by means of a short solenoid. This solenoid was made slightly longer than the iron rods, so that a more uniform field might be obtained. With it, fields up to 600 gauss were available. The inside of the solenoid was fitted with a double lining for a water cooling system. This was essential, as the coil became quite warm when heavy currents were used, and it was necessary to keep the temperature of the rod nearly constant. A change of temperature of the rod of one degree would produce an elongation of the same order as the magnetostrictive effect. As will be seen from the method of procedure, small gradual thermal expansions did not interfere with the measurement of the magnetostrictive change in length.

As the magnetizing solenoid was longer than the iron rod it was necessary to solder short pieces of brass rod to each end. This was done holding the pieces in a lathe, so that accurate alignment of the three parts could be obtained. The brass rod at one end was turned down to a fine point, on which the lever bore. The other end was provided with a 10 B.A. thread. This composite

rod was screwed into the end of a large brass rod, which could be slid into a close fitting brass collar and held there by set-screws. The axis of this collar was made to coincide with the axis of the magnetizing solenoid, so that the iron rod could be easily put into place in the centre of the solenoid. In this way the iron rods could be interchanged without disturbing the solenoids or the magnetometer.

To measure the magnetization, a magnetometer was used. This was provided with an astatic system, made by attaching two small magnets about 2 mms. long and $1/10$ mm. thick to a fine glass rod. These magnets were placed parallel, but in opposite directions, and at a distance from one another approximately equal to the length of the iron rods. A small mirror was also attached to the glass rod. The whole was then suspended by a fine glass fibre in a closed glass tube, provided with a window. Its position was adjusted so that the magnets were approximately on the same levels as the ends of the iron rod. With this arrangement the action of the poles at the end of the rod was additive, and the effect of extraneous fields eliminated. The magnetometer was used in a null way. The magnetizing solenoid was balanced by a similar coil connected in series with it, and placed on the opposite side of the magnetometer. The position of this coil was carefully adjusted till the effect of the magnetizing solenoid was annulled for all values of the magnetizing current used. It was almost impossible to get an absolute balance for all current strengths, but the remaining effect was always small compared to that of the magnetized iron rod. A third coil (not shown in figure) was used to balance the magnetic effect of the iron rod. The current through this coil was measured, and it was assumed that the moment of the iron rod was, at any time, proportional to the current through it. To reduce the measurements to absolute values, calibration was effected by substituting for the iron rod a small permanent magnet of about the same dimensions and measuring the current necessary to balance it. The magnetic moment of this permanent magnet was found by the Gauss method. The zero position of the magnetometer was measured by using a lamp and scale in conjunction with the mirror on the suspension.

The apparatus was fixed to a heavy brass plate to secure rigidity, and this, in turn, on a heavy wooden plank resting on three tennis balls and loaded down with lead weights. This step was necessary to reduce vibrations, which disturbed the image in the telescope.

§ 3. *Procedure.*

The magnetizing solenoid and its counterpart were first adjusted, and the coil compensating the iron rod calibrated, as described above. The iron rod was then put into place so that it occupied a central position in the magnetizing solenoid. The rod was magnetized to the desired amount, and when the magnetometer suspension was brought back to its zero position, the current in the compensating coil measured. The magnetizing circuit was then broken and the telescope sighted. The circuit was made and the accompanying motion of the scale measured. As soon as the deflected position of the scale was noted, the circuit was broken and the zero position of the scale checked. This operation was repeated till the apparent scale motion was accurately determined.

The magnetizing circuit was at first made and broken by a knife-switch. In this case it was found that the scale did not return to its zero position when the circuit was broken. This was apparently due to heating caused by currents induced in the iron by the sudden application of the magnetic field. To avoid this difficulty, a sliding resistance used as a potentiometer was used to make and break the magnetizing circuit. This method increased the period of building up of the field and reduced the Foucault currents, so that the thermal expansion due to this cause was negligible. When heavy currents were used in the magnetizing solenoid, the water cooling system was not sufficient to prevent a small transfer of heat to the iron rod. This caused a small gradual shift of the scale zero. But as the time between the making and the breaking of the current was small, the zero shift in this period was small and could be eliminated by taking, as the zero, the mean of the zero positions before and after. Readings were taken in this way with different field strengths, up to those sufficient to give approximate saturation. When the series of measurements was finished, the iron rod was removed and the balance of the magnetizing coils checked.

No precautions were taken to eliminate hysteresis. The magneto-strictive elongation did not seem to depend on the previous magnetic treatment, and the remanent magnetization was always small, less than $\frac{1}{2}$ per cent. of the saturation value.

The length of the iron rod was measured with a travelling microscope, and the volume determined by weighing, and assuming a density of 7.86 gms. per c.c.

§ 4. *Accuracy.*

The relative values of any series of measurements was fairly good; for any rod the readings could be repeated quite consistently. But it was difficult to determine absolute values with any great degree of accuracy.

In measuring the elongation the chief error was in determining the magnification, the chief difficulty lying in the measurement of the distance between the fixed knife-edge and the point on which the lever bore. The distance between the edge and the centre of the inside tube of the solenoid was measured with a travelling microscope. Each rod was then carefully centred in this tube; this could be done accurately as the clearance was only about $\frac{1}{2}$ mm. It was then assumed that the point of the rod lay on the axis of the tube. The point was probably not more than $\frac{1}{5}$ mm. from the centre, and as the distance to the knife-edge was 5.4 mms. the error is less than 4 per cent. The total absolute probable error in measuring the elongation is about 5 per cent.

The magnetic field was calculated from the constants of the magnetizing solenoid. But as the coil was short, the field fell off considerably near the ends. The field was calculated for points at different distances from the centre, and a value of 1,200 gauss per ampere taken as an average. It is probably correct to within 5 per cent. No attempt was made to measure the field more accurately, as it did not seem of great importance.

The measurement of the magnetization was subject to several errors. The moment of the permanent magnet, used for calibration, could be found to less than 2 per cent., and the current in the compensating coil adjusted and measured with an error of about 1 per cent. There are, however, other possible sources of error. In computing the magnetic moments of the iron rods, it is assumed that for a given moment they all exert the same force on the magnetometer. As the length of the rods varied considerably, this is probably not true. Although, as the magnetometer was removed a distance more than twice the length of the rods, it is probably not a very serious error. Further, the rods may not have occupied exactly the same positions. The effect of moving the rods was investigated, and was found to be small for the small distance by which they might be removed from the central position. It seemed possible to assume that the effective magnetic moment of the compensating coil was proportional to the current through it, as it was some distance from the magnetometer. It is impossible to estimate the error due to these causes, but it may be remarked that, for the saturation values of the magnetic intensity, the deviation from the mean for all the rods was about $3\frac{1}{2}$ per cent. The error in the absolute values is probably not more than 5 per cent.

§ 5. *Results.*

Measurements were made on 12 rods in all; these were cut from several different crystals, along one of the directions given above. A rod of soft-iron

wire was also measured. The results obtained for different rods cut parallel to the same crystal direction were quite similar. Results will be given for three rods only, one parallel to each direction; and all cut from the same crystal. The particulars of these rods are given below:—

	Rod A.	Rod B.	Rod C.
Axis	1, 0, 0	1, 1, 0	1, 1, 1
Length	1.63 cms.	1.29 cms.	1.50 cms.
Weight	0.0920 gms.	0.0602 gms.	0.1023 gms.
Mean Area of			
Cross-Section	0.725 sq. mm.	0.585 sq. mm.	0.865 sq. mm.
Demag. Coeff. ..	0.155	0.195	0.205

The demagnetizing coefficients given were calculated as for an elongated spheroid of the same length and with a minor axis equal to the mean radius of the rod. (The rods used had an approximately square section, but were not uniform from end to end.) These values are not very reliable.

In Fig. 2 the I-H curves are shown for the three rods. It is noticed that after

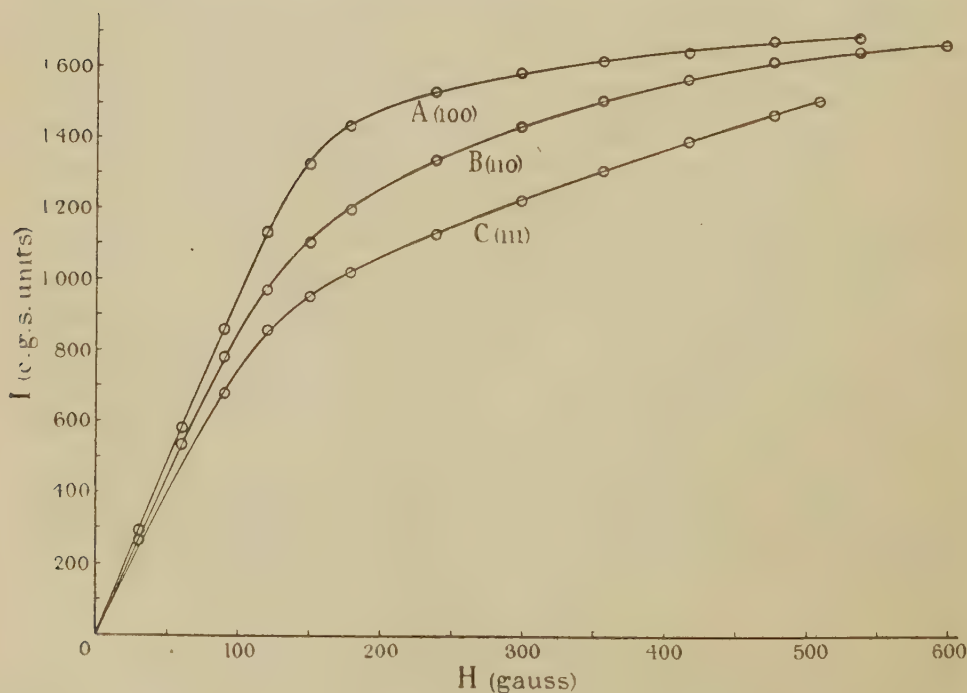


FIG. 2.

the initial rapid rise in magnetization, which is probably governed by the demagnetizing co-efficients, the saturation value for rods B and C is reached much more slowly than for rod A. This effect was observed with all the rods cut in these directions, and cannot be connected with any experimental errors. The saturation value is given by $I = 1,700$.

In fig. 3 the elongation, change in length per centimetre, is plotted as a function of the magnetic field, and in fig. 4 it is given as a function of the magnetic

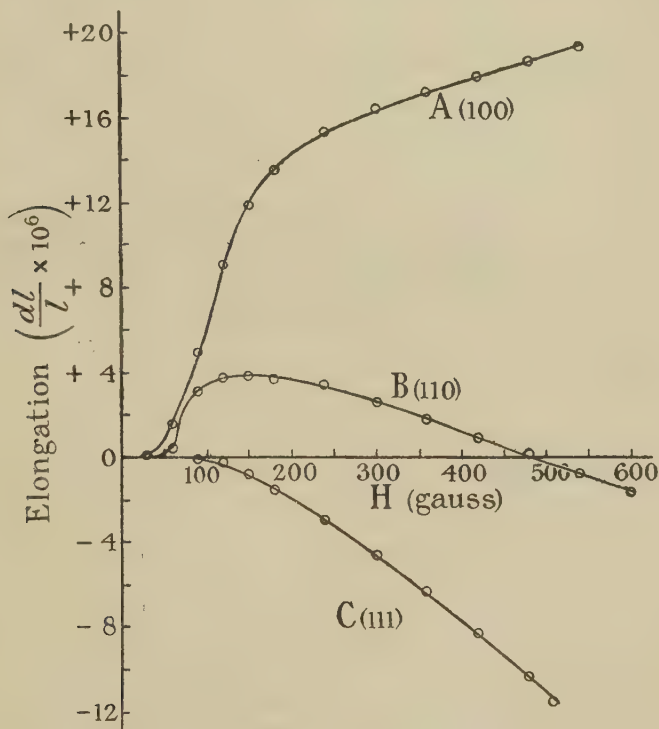


FIG. 3.

intensity. In this graph the curve for the soft-iron rod is given. The effect of crystal structure on magneto-striction is clearly shown in these graphs. With magnetization in the direction of the $(1, 0, 0)$ axis, the result is an increase in length, which becomes larger as the magnetization increases. On the other hand, for the $(1, 1, 1)$ axis there is a continuous decrease in the length of the specimen. For the $(1, 1, 0)$ axis the result is more complicated, and is very similar to that for the soft-iron rod. There is, at first, an increase in length; this is followed by a decrease as saturation is approached. It may be noted

that, as saturation is approached, the elongation tends to become an approximately linear function of the magnetic intensity.

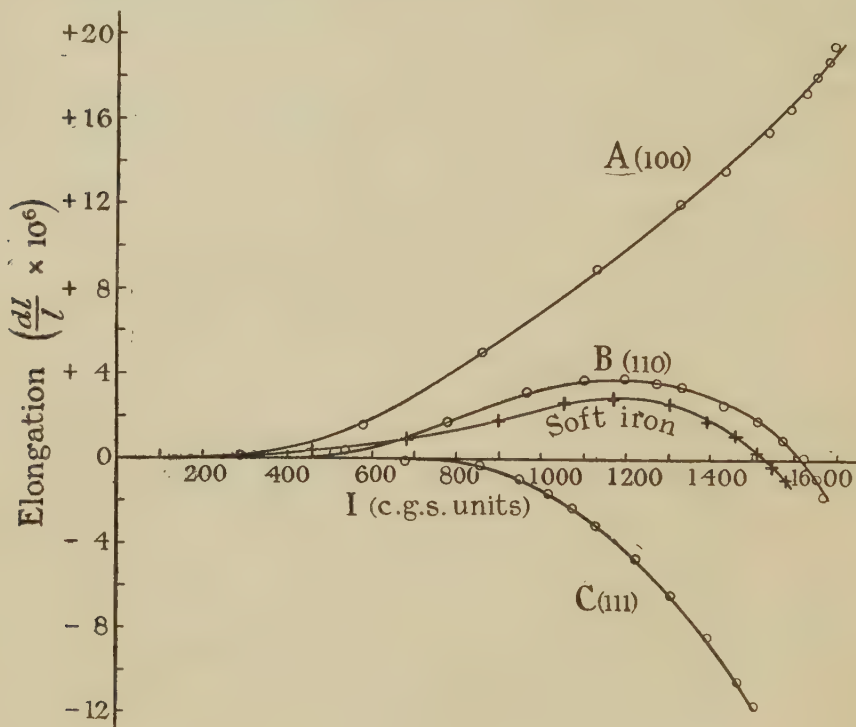


FIG. 4.

§ 6. Discussion.

In these experiments, there is a striking corroboration of the fact already found ('Roy. Soc. Proc.,' A, vol. 107, p. 496, 1925) that the iron crystal is most easily magnetized parallel to a (1, 0, 0) axis, and most reluctantly along the (1, 1, 1) axis. The magneto-strictive effect also seems to be modified in a more or less regular way as the tetragonal, binary and trigonal axes are considered in turn. This suggests the possibility that the molecular field, which was postulated in the paper mentioned above to account for the variation in the susceptibility of the crystal, may be due to the work involved in magnetostriction. It is interesting to note that the greatest increase in length is observed along the (1, 0, 0) axis, which corresponds to the direction of easiest magnetization in the crystal. But it is impossible to say whether the work involved in the magneto-striction phenomenon is greatest or least in this direc-

tion, as the deformation has only been measured in the direction parallel to the field. An estimate of the work done could only be obtained from a complete knowledge of the nature of the deformation of the crystal lattice.

The phenomenon of magneto-striction is probably due to the orientation of the atoms in the magnetic field. The forces of coherence which hold the atom in the crystal lattice have probably not a spherical symmetry, and consequently the orientation of the atoms might be expected to give rise to a change of dimensions of the kind observed in this phenomenon. This view is supported by the fact that the magneto-striction increases permanently with the magnetization, and gives no indication of tending towards a saturation value, when plotted against the intensity of magnetization. It seems possible to obtain a rough explanation of the results found, by giving the field of force of the atom a distribution corresponding to the shape of an oblate spheroid, with the axis of revolution coinciding with the direction of the magnetic moment of the atom.

It is interesting to note that the shape of the curve for soft iron can be explained by the combination of the different types of effects found for single crystals. In soft iron there is probably a heterogeneous mass of small crystals, with a random distribution of their axis. (In the case of iron wire which has been drawn, this last assumption is not strictly true.) The initial increase in length for soft iron would be expected, as it is seen that the increase in length begins at an earlier stage than the contraction. The final contraction is explained by the fact that only the few elementary crystals having a tetragonal axis near the axis of the iron rod would contribute to the general effect, an increase in length when saturation is approached, and that this contribution would be overwhelmed by the contraction effect of the rest of the rod. The values of the elongation obtained for the crystals are larger than the values ordinarily obtained with soft iron. This is to be expected, as in this case, the whole of the rod will give an effect in the same direction. It is seen that the magneto-striction effect will depend very greatly on the exact crystalline structure of the specimen examined, and will be greatly changed by any treatment which alters the crystal structure.

§ 7. *Effect of Stress on Magnetization.*

Some further experiments were done on the effect of stress on magnetic intensity, with regard to the effect of crystal structure. The results obtained were applied to a reciprocal relation between this effect and magneto-striction. This relation is deduced thermo-dynamically, so that the agreement obtained gives an indication of the accuracy of the experiments.

This relation has been discussed, and tested experimentally, by Honda and Terada ('Phil. Mag.,' vol. 14, p. 65, 1907). The appropriate equation is given in the form :—

$$\frac{\partial e}{\partial H} = \frac{\partial I}{\partial T} + \frac{2\pi}{E} \times \frac{\partial I^2}{\partial H},$$

where e is the change in length per unit length,

T is the force per unit area applied,

E is the value of Young's modulus, taken as that for wrought iron
($= 2 \times 10^{12}$), and

I and H are the magnetic intensity and magnetic field.

In this equation, the second term on the right is an extra term, deduced by Gans and Sano, arising from the assumption that the lines of magnetic induction issue normally from the ends of the rod. The authors of the paper quoted above find better agreement if this term is omitted, and suggest that in their experiments on long wires, this assumption is not fulfilled. This question will be referred to later.

This term and the value of that on the left can be found from the experiments already described. The other term is obtained from the following experiment.

Apparatus.

The same apparatus as in the previous experiment is used with slight modifications. The magnification system was removed, and a heavy wooden beam rigidly supported over the top of the magnetizing solenoid. From this, by means of a thick brass rod, into which it was screwed, the composite iron and brass rod was supported so that the iron rod was inside the solenoid in the same position as in the previous experiment. At the lower end was attached a strong cord. This passed over two pulleys; the first of which was below and on the axis of the solenoid, and then to a pan in which weights could be placed. It was important to make the beam very solid to prevent it sagging when the weights, several kilograms, were applied. Such an effect would allow the iron rod to be dragged down bodily causing the magnetometer to show a false change of magnetic intensity. A 200 gms. weight was kept in the pan throughout so that the system was always under a slight stress, and the position of the iron rod fairly constant.

To measure the magnetic intensity, the magnetometer and the compensating coil were used as before. The magnetometer was suspended with a very fine quartz fibre so that its sensitivity was greatly increased. The small changes of intensity occurring when the stress was applied, were measured by the resulting

deflection of the magnetometer, the current in the compensating coil being kept constant. The deflection of the magnetometer was calibrated by varying the current in the compensating coil, and finding the corresponding deflection of the magnetometer. Calibration was made with the magnetizing solenoids excited to different degrees. This was necessary, due to the change in the gradient of the magnetic field around the magnetometer, as the current in the magnetizing solenoids was changed. The accuracy with which the change in intensity could be measured was not very high, due to the smallness of the effect. For rod A, which gave a fairly large change, the probable error is about 10 per cent.; for the other rods the effect is very much smaller and the error larger.

Results.

Experiments were done on most of the rods used before, but results will only be given for the three rods described above.

The iron rod was magnetized, and the compensating coil made to balance. Weights were then applied and the resulting deflection of the magnetometer measured. This process was repeated for different magnetic fields, and for each the effect of $\frac{1}{2}$, 1 and 2-kilogram weights was measured. The results are shown in fig. 5.

The effect of increasing the magnetization, keeping the load constant, was

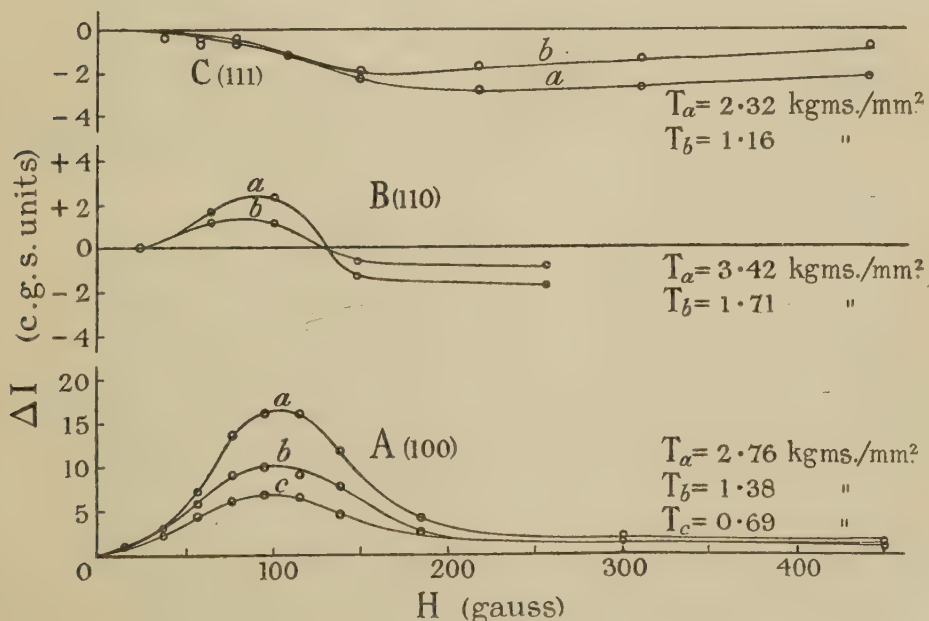


FIG. 5.

investigated. The results were not so accurate, as the sensitive differential method could not be applied; but they agreed within experimental error with the values deduced in the other way.

The effect of crystal structure on the change of magnetic intensity by stress is very marked. It agrees with the effect found for magneto-striction. In the case of rod A, there is an increase in magnetic intensity when the rod is pulled corresponding to the increase of length with magnetization. For rod C, the effect is the converse. And for rod B, the change of sign of the effect appears as in the case of magneto-striction. The interpretation of these results is probably not as simple as in the case of magneto-striction, as in this case there may be an indefinite amount of yielding along slip planes.

In the table, the values of the separate terms of the reciprocal relation are given for the three rods for different field strengths. The ratios of the two sides of the equation are also given. The agreement in the case of rods A and B is quite good, especially for the weaker fields. For strong fields, where the agreement is not as good, it may be that the assumption that the lines of magnetic induction issue normally to the ends of the rods breaks down. This might be expected to occur as the induction increases when magnetic saturation is approached. In addition to this source of uncertainty in the value of the term $\frac{2\pi}{E} \times \frac{\partial I^2}{\partial H}$, it must be pointed out that the value of Young's modulus taken is probably not that for a single crystal of iron, and also that its value may vary considerably for different directions in the crystal. Taking these sources of error into consideration, the agreement seems to be quite within the experimental error anticipated.

§ 8. *Summary.*

The magneto-strictive effect is measured in single crystals for three directions, the tetragonal, binary and trigonal axes. The effect along each direction is found to be different, and it is shown that, by combination of the different effects, the magneto-strictive effect in soft iron may be satisfactorily explained.

A connection between magneto-striction and the molecular field found in iron crystals is suggested, and the nature of the magneto-strictive change of dimensions discussed.

A reciprocal relation between magneto-striction and the effect of stress on magnetization is investigated, experimentally, and the agreement found to be satisfactory.

In conclusion, I should like to express my thanks to Prof. Sir Ernest Rutherford for his interest in this work ; to R. L. Aston, of this laboratory, for his X-ray analysis of the crystals used ; and especially to Dr. P. Kapitza for many suggestions as to the experimental work, and very helpful discussion of the results.

On the Forces between Atoms and Ions.

By J. E. LENNARD-JONES,* Ph.D., Trinity College, Cambridge.

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§ 1. *Introduction.*

The ultimate knowledge which we can hope to derive from many of the physical properties of gases and crystals is that which concerns the nature of the forces between the constituent atoms and ions. In terms of these forces many diverse phenomena both of gases and solids should be explicable. In some recent researches† the writer has sought to determine the repulsive part of the forces between certain atoms and ions in terms of inverse power laws. This representation is considered superior to the treatment of atoms and ions as rigid spheres with definite diameters, as is generally done, for it permits of the correlation of the physical properties of a gas with those of certain associated crystals. Thus the forces which explain the thermal conductivity of neon have been shown to explain as well the observed spacing constants of crystals like NaF and MgO.

These researches had their starting point in an investigation of certain physical properties of the pure gases, and this formed a necessary preliminary step to the later work on crystals. The methods there developed were, however, applicable only to neon and argon, for only in those cases was the necessary experimental information available. Consequently the later extension to include the forces of ions applied only to ions of similar electronic structure to these gases.

The object of the present paper is to extend the scope of the preceding papers to include krypton-like and xenon-like ions. This is done by deducing

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† 'Roy. Soc. Proc.,' A, vol. 106, pp. 441, 463, 709 ; vol. 107, p. 157 (1924-25) ; J. E. Lennard-Jones and P. A. Taylor, 'Roy. Soc. Proc.,' A, vol. 109, p. 476 (1925).

the fields of krypton and xenon from crystal observations alone. Thus the only information necessary for krypton is the interatomic distance and compressibility of Rb Br, together with the refractivities of Br^- , Kr and Rb^+ . From the fields of krypton and xenon those of the associated ions are derived. The methods of the preceding paper are then used to deduce the fields between any two of a series of neon-like, argon-like, krypton-like and xenon-like ions. The results represent a first attempt at the numerical evaluation of force constants.

Applications of the results are then made to evaluate the interatomic distances of a number of crystals. In all 32 crystals have been dealt with, including 16 alkaline halogens. In the case of the latter, the calculated values are found to lie, with one exception, within 1 or 2 per cent. of the observed distances. Calculations are also made of the compressibilities and crystal energies of these crystals, and are found to be in satisfactory agreement with the values observed.

§ 2. *The Nature of the Repulsive Fields of Krypton and Xenon.*

Wasastjerna,* in recent papers, has found the ionic refractivities of a number of ions, and has deduced from the results on certain plausible assumptions the relative sizes of ions and atoms, so that from a knowledge of the kinetic-theory diameter of a pure gas, like neon, those of ions of similar structure can be deduced. In this and preceding investigations† the repulsive fields of atoms are no longer represented by rigid spheres, but more generally by inverse power laws. Nevertheless, a method has been devised of using Wasastjerna's work to pass from the force constant of a pure gas atom to that of an ion of similar electronic structure.‡

Briefly, if the one be denoted by λ_0 and the other by λ_1 , while the relative sizes as given by Wasastjerna§ be x , then

$$\lambda_1 = x^{n-1}\lambda_0, \quad (2.01)$$

where n is the index of the repulsive field, the assumption being made that cores of the same electronic structure repel according to the same law. The values of x given by Wasastjerna are reproduced in Table I. For any pure gas atom and its associated ions there are therefore virtually only two unknowns, viz., the value of n and the force constant of the atom λ_0 .

We proceed first to the determination of n for each group.

* Wasastjerna, 'Soc. Scient. Fenn. Comm. Phys. Math.,' vol. 1, p. 38.

† 'Roy. Soc. Proc.,' *loc. cit.*

‡ J. E. Lennard-Jones and P. A. Taylor, *loc. cit.*, § 2.

§ Wasastjerna, 'Soc. Scient. Fenn. Comm. Phys. Math.,' vol. 1, p. 38.

Table I.—The Relative Sizes of Ions and Atoms (Wasastjerna).*

$\frac{\rho^{--}}{\rho}$	$\frac{\rho^-}{\rho}$	$\frac{\rho}{\rho}$	$\frac{\rho^+}{\rho}$	$\frac{\rho^{++}}{\rho}$
O ⁻⁻ 1.445	F ⁻ 1.240	Ne 1.00	Na ⁺ 0.938	Mg ⁺⁺ 0.817
S ⁻⁻ 1.386	Cl ⁻ 1.205	Ar 1.00	K ⁺ 0.912	Ca ⁺⁺ 0.838
Se ⁻⁻ 1.264*	Br ⁻ 1.173	Kr 1.00	Rb ⁺ 0.919	Sr ⁺⁺ 0.856
Te ⁻⁻ 1.169*	I ⁻ 1.152	Xe 1.00	Cs ⁺ 0.922	Be ⁺⁺ 0.853

* Wasastjerna, 'Soc. Scient. Fenn. Comm. Phys. Math.,' vol. 2, p. 7 (1924).

The compressibility of a face-centred crystal of the rock-salt type, defined in the usual way as the specific change of volume with pressure $\left(\kappa = \frac{1}{v} \frac{dv}{dp}\right)$, can be shown to be given by*

$$\frac{1}{\kappa} = \frac{1}{3 \cdot 6} \left\{ \frac{(n_{11} - n_{12}) \lambda_{n_{11}} A''_{n_{11}-1}}{a^{n_{11}+2}} + \frac{(n_{22} - n_{12}) \lambda_{n_{22}} A''_{n_{22}-1}}{a^{n_{22}+2}} + \frac{(n_{12} - 2) (3 \cdot 495) e^2 z^2}{a^4} \right\} \quad (2.02)$$

where $\lambda_{n_{11}} r^{-n_{11}}$ is the force assumed between kations, $\lambda_{n_{22}} r^{-n_{22}}$ that between anions and $\lambda_{n_{12}} r^{-n_{12}}$ that between a kation and an anion, and a is the distance between kation and anion; e is the usual electrostatic charge, and z the valency; A''_s is a number depending only on s , and represents a triple summation over the lattice points of the system,† while the number $3 \cdot 495$ is also the value of a triple summation, computed by Madelung‡ and Emersleben.§

This formula simplifies considerably when the kation and anion have the same structure, for then $n_{11} = n_{22} = n_{12}$, and the formula reduces to its last term. Taking the experimental value of $8 \cdot 2 \cdot 10^{-12}$ for the compressibility of Rb Br, as given by Richards and Saerens,|| and the value $3 \cdot 430 \text{ \AA}$ as its crystal constant,¶ we find $n = 9 \cdot 6$. If we confine ourselves to integral values only of n , we may take as the effective value for the krypton group, $n = 10$.

* J. E. Lennard-Jones and P. A. Taylor, 'Roy. Soc. Proc.,' A, vol. 109, p. 476 (1925).

† J. E. Jones and A. E. Ingham, 'Roy. Soc. Proc.,' A, vol. 107, p. 636 (1925).

‡ Madelung, 'Phys. Zs.,' vol. 19, p. 524 (1918).

§ Emersleben, 'Phys. Zs.,' vol. 24, pp. 73 and 97 (1923).

|| Richards and Saerens, 'Journ. Amer. Chem. Soc.,' vol. 46, p. 934 (1924).

¶ Davey, 'Phys. Rev.' (2), vol. 21, p. 143 (1923), gives $3 \cdot 418 \text{ \AA}$, and Spangenberg, 'Zs. f. Kryst.,' vol. 57, sect. 5 (1923), gives $3 \cdot 440 \text{ \AA}$.

In the same way, the value of n for the xenon group may be found from the compressibility of CsI. This, however, is a body-centred cubic, and so the above formula is not applicable. In this case, we find*

$$\frac{1}{\kappa} = V \frac{dp}{dV} = \frac{1}{18a} \frac{d^2\phi_0}{da^2} \quad (2.03)$$

where a is the length of unit cube and ϕ_0 is the potential of one cell due to all the rest, given by

$$\begin{aligned} \phi_0 = & \frac{\lambda_{n_{11}} A_{n_{11}-1}}{(n_{11}-1) a^{n_{11}-1}} + \frac{\lambda_{n_{22}} A_{n_{22}-1}}{(n_{22}-1) a^{n_{22}-1}} \\ & + \frac{2\lambda_{n_{12}} \left[\frac{2^{n_{12}-1}}{3^{(n_{12}-1)/2}} B_{n_{12}-1} - A_{n_{12}-1} \right]}{(n_{12}-1) a^{n_{12}-1}} + \phi_0^{(e)}; \end{aligned} \quad (2.04)$$

in this formula B_s , like A_s , is a triple summation over the points of a certain lattice system and has been defined in a former paper,[†] while the term $\phi_0^{(e)}$ represents the electrostatic contribution to the energy, its value having been shown to be‡

$$\phi_0^{(e)} = - \frac{2e^2 (2 \cdot 035)}{a}. \quad (2.05)$$

From these equations, using the fact that $\partial\phi/\partial a = 0$, it is easy to deduce that

$$\begin{aligned} \frac{1}{\kappa} = & \frac{1}{18a^4} \left\{ \frac{(n_{11}-n_{12})\lambda_{n_{11}} A_{n_{11}-1}}{a^{n_{11}-2}} + \frac{(n_{22}-n_{12})\lambda_{n_{22}} A_{n_{22}-1}}{a^{n_{22}-1}} \right. \\ & \left. + 2(n_{12}-2)e^2 (2 \cdot 035) \right\} \end{aligned} \quad (2.06)$$

Here again there is considerable simplification when $n_{11} = n_{22} = n_{12}$. This is the case for CsI, and so, taking the observed values $9 \cdot 3 \cdot 10^{-12}$ for κ § and $4 \cdot 558 \text{ \AA}$ for a ,|| we get $n = 11 \cdot 005$. The value $n = 11$ is then assumed for xenon and the group of ions Te^{--} , I^- , Cs^+ and Ba^{++} .

§ 3. The Force Constants of Krypton and Xenon and Associated Ions.

The formula for the interatomic distance of a face-centred cubic has been shown in a former paper to be¶

$$\frac{\lambda_{n_{11}} A''_{n_{11}-1}}{a^{n_{11}}} + \frac{\lambda_{n_{22}} A''_{n_{22}-1}}{a^{n_{22}}} + \frac{2\lambda_{n_{12}} A'_{n_{12}-1}}{a^{n_{12}}} = \frac{(3 \cdot 495) e^2 z^2}{a^2} \quad (3.01)$$

* Born, 'Atomtheorie des festen Zustandes,' p. 569, 2nd Aufl. (1923).

† J. E. Jones and A. E. Ingham, *loc. cit.*, p. 638.

‡ Born, *loc. cit.*, p. 747.

§ Richards and Saerens, *loc. cit.*

|| W. H. Bragg and W. L. Bragg, 'X-rays and Crystal Structure,' p. 306 (1924).

¶ J. E. Lennard-Jones and P. A. Taylor, *loc. cit.*, p. 487.

in a notation already explained. In the case of Rb Br, this reduces to

$$a^{n-2} = \frac{A''_{n-1} (\lambda_{11} + \lambda_{22}) + 2A'_{n-1} \lambda_{12}}{(3 \cdot 495) e^2 z^2}. \quad (3.02)$$

We have already observed that λ_{11} and λ_{22} are connected with λ_{00} (the force constant of Kr) by the relation

$$\lambda_{11} = x^{n-1} \lambda_{00}, \quad \lambda_{22} = y^{n-1} \lambda_{00}, \quad (3.03)$$

where x and y are the Wasastjerna-ratios, and, in the same way, we have given arguments for supposing that*

$$\lambda_{12} = [\tfrac{1}{2}(x + y)]^{n-1} \lambda_{00}. \quad (3.04)$$

It follows that λ_{00} may be deduced from the observed value of a from the equation

$$\lambda_{00} = \frac{(3 \cdot 495) e^2 z^2 a^{n-2}}{A''_{n-1} (x^{n-1} + y^{n-1}) + 2A'_{n-1} \left(\frac{x+y}{2}\right)^{n-1}}. \quad (3.05)$$

In the case of Rb Br, we have $n = 10$, $x = 0 \cdot 919$, and $y = 1 \cdot 173$ from Table I, while $a = 3 \cdot 430 \text{ \AA}$. We thus find $\lambda_{00} = 7 \cdot 340 \cdot 10^{-80}$. The force constants of the associated ions are given in Table II.

Table II.—The Force Constants of the Krypton-group (force of the type λr^{-n} with $n = 10$; λ is given in the table in such units as give the force in dynes, when the unit of length is 1 $\text{\AA}$).

Se ⁺⁺	Br ⁻	Kr	Rb ⁺	Sr ⁺⁺
60·52	30·86	7·340	3·431	1·812

In a similar way, the force constants of the xenon group can be deduced from the measurement of CsI, but this, being a body-centred cubic, requires the use of formula

$$\frac{\lambda_{n11} A_{n11-1}}{a^{n11}} + \frac{\lambda_{n22} A_{n22-1}}{a^{n22}} + \frac{2\lambda_{n12}}{a^{n12}} \left[\frac{2^{n12-1}}{3^{(n12-1)/2}} B_{n12-1} - A_{n12-1} \right] = \frac{2(2 \cdot 035) e^2}{a^2} \quad (3.06)$$

instead of equation (3.01), and the force constant of xenon then follows from the equation

$$\lambda_{00} = \frac{2(2 \cdot 035) e^2 a^{n-2}}{A_{n-1} (x^{n-1} + y^{n-1}) + 2 \left(\frac{x+y}{2}\right)^{n-1} \left[\frac{2^{n-1}}{3^{(n-1)/2}} B_{n-1} - A_{n-1} \right]} \quad (3.07)$$

* J. E. Lennard-Jones and P. A. Taylor, *loc. cit.*, p. 487.

In this case $n = 11$, $a = 4.558 \text{ \AA}$, $x = 0.922$, $y = 1.152$, and so we obtain $\lambda_{00} = 6.214 \cdot 10^{-87}$. The force constants of the xenon-like ions are deduced to be as given in Table III.

Table III.—The Force Constants of the Xenon-group* ($n = 11$).

Te ⁻⁻⁻	I ⁻	Xe [.]	Cs ⁺	Ba ⁺⁺
296.16	255.81	62.142	27.586	12.672

For completeness, the corresponding results for the neon and argon results may also be included.†

Table IIIA.—The Force Constants of the Neon and Argon groups ($n = 11$ and 9 respectively).

O ⁻⁻	F ⁻	Ne	Na ⁺	Mg ⁺⁺
17.66	3.82	0.444 ₆	0.234	0.058 ₉

S ⁻⁻	Cl ⁻	A	K ⁺	Ca ⁺⁺
13.75	4.48	1.009	0.483	0.245

§ 4. The Interaction of Ions of different Groups.

The forces found up to now apply only to particles (whether atoms or ions) of the same kind, and the question now arises as to how the results can be generalised to give the forces between ions of different kinds. We may consider first the forces between atoms alone. The values of the index n (in λr^{-n}), which have now been found† are

	Ne	A	Kr	Xe
$n =$	11	9	10	11

The index of repulsion between an argon and a neon atom was taken in the preceding paper† to be midway between that of argon-argon and neon-neon. In the same way that of argon-xenon can also be taken to be 10.

In the other cases, where, for instance, Kr is concerned, the mean value of the n 's is non-integral. It avoids complication if integral values be chosen, and the question is which to take. In these cases the n for krypton was

* See note to Table II.

† J. E. Lennard-Jones and P. A. Taylor, *loc. cit.*, p. 487.

regarded as 9.6, as it was actually found to be, and that integer was chosen which was nearest to the mean value of this and the other value of n . Actually in the calculation both possible values were used throughout, to find the sort of modification introduced, if any. This was found to be unimportant.

In this way, the following scheme can be drawn up, indicating the *type* of the forces between any two of the pure gases, and inferentially that of the corresponding ions.

Table IV.—The Law of Force between Atoms (the values of n in λr^{-n}).

	Ne	A	Kr	Xe
Ne	11	10	10	11
A	10	9	10	10
Kr	10	9	10	10
Xe	11	10	10	11

To find the force constants appropriate to these laws of force, we use the method already described in the preceding paper.* We there found a generalised “diameter” connected with the force constant by the expression,

$$\sigma^{(n)} = \left[\frac{\lambda_n}{(n-1)W} \right]^{1/n-1} \quad (4.01)$$

and, since λ_n is a function of n , $\sigma^{(n)}$ is a function of n and the arbitrary constant W only. The latter determines the scale on which the “diameters” are measured. Its choice makes no difference to the results finally obtained.* It is here taken to be $3k/2$ to preserve uniformity with preceding papers.† The function $\sigma^{(n)}$ was treated in the same way in which the diameter of a rigid sphere is used. Thus we regard the generalised “radii” as additive, and write

$$\sigma_{12}^{(n)} = \frac{1}{2} (\sigma_{11}^{(n)} + \sigma_{22}^{(n)}) \quad (4.02)$$

with the inference that

$$\lambda_{12}^{1/(n-1)} = \frac{1}{2} (\lambda_{11}^{1/(n-1)} + \lambda_{22}^{1/(n-1)}). \quad (4.03)$$

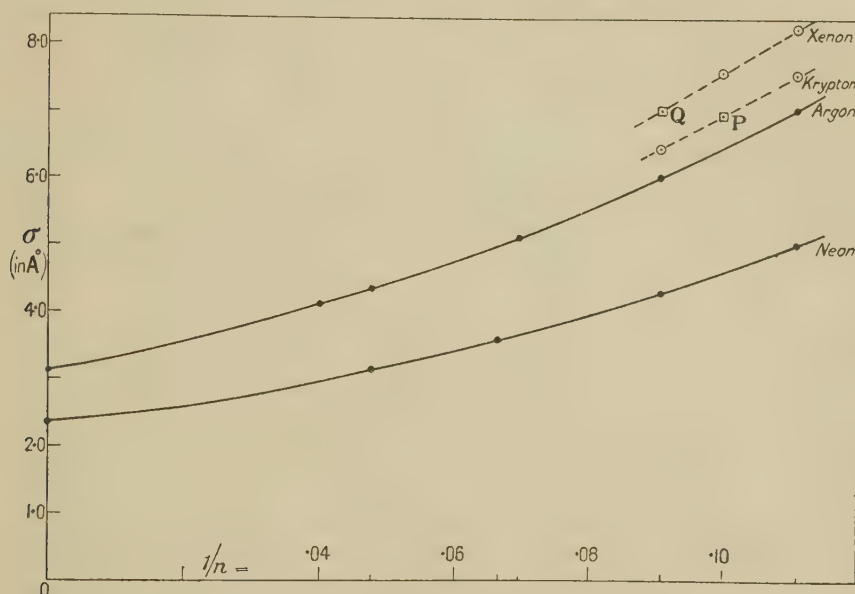
It is to be observed, however, that the formula (4.02) is applicable only when all the σ 's are functions of the same n . A difficulty arises when λ_{11} is known for only one value of n , as it is for krypton ($n = 10$), and λ_{22} for another as for xenon ($n = 11$). This did not occur in the cases of neon and argon,‡ for

* Cf. Lennard-Jones and Taylor, *loc. cit.*

† ‘Roy. Soc. Proc.,’ A, vol. 106, p. 452 (1924); k is the usual Boltzman constant and $3k/2$ is the kinetic energy of a molecule at 1° absolute.

‡ ‘Roy. Soc. Proc.,’ A, vol. 106, p. 463; vol. 107, p. 157 (1925).

the σ 's were obtained for several values of n , so that they could be represented graphically as in the figure, and other values deduced by interpolation if necessary.



The "diameters" of atoms.

The similarity of the curves for neon and argon justifies us in inferring similar curves for krypton and xenon. Through the known points P and Q, deduced from the values of λ_{00} given above, the curves (shown dotted in the figure) have been conjectured. These are drawn so that any ordinate intersects the four curves in the same ratio.* Corresponding to the values 9, 10 and 11 of n , the "diameters" given in Table V are obtained.

Table V.—"Diameters" of the Pure Gases ($\sigma^{(n)}$).

n	Ne	A	Kr	Xe
9	5.02	7.05	7.58	8.26
10	4.63	6.50	6.98	7.60
11	4.30	6.03	6.49	7.05

From this information it is easy to deduce the results of Table VI, giving the forces between any two atoms.

* Support for this procedure may be found in the fact that the ratios of corresponding ordinates of the curves for neon and argon are approximately constant.

Table VI.—The Repulsive Forces between Pure Gas Atoms.*

	Ne	A	Kr	Xe
Ne	0.4446	0.950	1.391	7.144
A	0.950	1.009	1.351	7.979
Kr	1.391	1.351	7.340	10.80
Xe	7.144	7.979	10.80	62.142

In a similar way the forces between certain ions can be found. The index of the law of force is as given in Table VII, inferred from Table IV.

Table VII.—The Law of Force between Ions. (The value of n in λr^{-n} .)

	F ⁻	Cl ⁻	Br ⁻	I ⁻
	O ⁻⁻	S ⁻⁻	Se ⁻⁻	Te ⁻⁻
Na ⁺ , Mg ⁺⁺	11	10	10	11
K ⁺ , Ca ⁺⁺	10	9	10	10
Rb ⁺ , Sr ⁺⁺	10	9	10	10
Cs ⁺ , Ba ⁺⁺	11	10	10	11

For these ions there can be drawn curves, such as those of our figure above, giving their generalized "diameters" as functions of n . They are obtained by multiplying the ordinates of the inert gas curves by the ratios given in Table I.† Table VIII contains some particular values which are required in the calculations.

Table VIII.—"Diameters" of Ions ($\sigma^{(n)}$).

n	F ⁻	Na ⁺	Cl ⁻	K ⁺	Br ⁻	Rb ⁺	I ⁻	Cs ⁺
9	6.23	4.71	8.50	6.43	8.89	6.96	9.52	7.61 ₆
10	5.74	4.34	7.83	5.93	8.19	6.41	8.75 ₅	7.01
11	5.33	4.03	7.27	5.50	7.61	5.96	8.12	6.50

n	O ⁻⁻	Mg ⁺⁺	S ⁻⁻	Ca ⁺⁺	Se ⁻⁻	Sr ⁺⁺	Te ⁻⁻	Ba ⁺⁺
9	7.26	4.10	9.77 ₅	5.91	9.58	6.49	9.66	7.05
10	6.69	3.78	9.01	5.45	8.83	5.98	8.88	6.48
11	6.21	3.51	8.36	5.05	8.20	5.55 ₅	8.24	6.01

* The force considered is of the type λr^{-n} , the appropriate values of n being given in Table IV; the units used for λ are those described in Table II. The question as to whether the law of force operative at small distances, as between neighbouring ions in crystals, is operative also at large distances is discussed in a previous paper ('Roy. Soc. Proc.,' A, vol. 108, p. 503).

† See note on p. 591.

By the application of formulæ (4.01) and (4.02) to these figures, the force constants given in Tables IX and X are derived.

Table IX.—The Force Constants between Monovalent Ions.*

	F ⁺	Cl ⁻	Br ⁻	I ⁻
Na ⁺	1.05	2.01	2.768	14.16
K ⁺	1.37	1.59	1.957	11.49
Rb ⁺	2.09 ₄	2.09 ₇	11.00	15.38
Cs ⁺	10.81	12.61	15.68	255.81

The tables are to be used in conjunction with Table VII.

Table X.—The Force Constants between Divalent Ions.*

	O ⁺⁺	S ⁺⁺	Se ⁺⁺	Te ⁺⁺
Mg ⁺⁺	1.53	3.14	2.923	10.13
Ca ⁺⁺	1.95	2.36	2.135	9.232
Sr ⁺⁺	3.045	3.151	12.40	12.82
Ba ⁺⁺	15.03	18.61	16.75	69.33

§ 5. Application of the Force Constants.

The force constants just derived can be applied to the calculation of a number of crystal properties, and a comparison of the results with observation constitutes an immediate check. Thus the interatomic distances of a number of crystals of the rock-salt type can be calculated, assuming, as usual, that the valency electron of the kation is absorbed into the electronic system of the anion, and that the electrostatic charges, alternately positive and negative, act as the forces of cohesion. The equilibrium between the electrostatic forces and the forces of repulsion discussed in this paper determines the size of the crystal cell. The appropriate formula has already been given, equation (3.01). It is solved for a by writing it in the form

$$(3.495) e^2 z^2 a^{n_{12}-2} \\ = 2A'_{n_{12}-1} \lambda_{12} + \lambda_{11} A''_{n_{11}-1} a^{n_{12}-n_{11}} + \lambda_{22} A''_{n_{22}-1} a^{n_{12}-n_{22}}, \quad (5.01)$$

and calculating a first approximation by neglecting the second and third terms on the right-hand side. This result is then used to make further approximations. These converge very rapidly, the difference between the second and third being only in the third decimal place.†

* See footnote, p. 592.

† The approximations to a for KI were, for example, 3.392, 3.476, 3.474.

Four of the alkaline halogens RbF, CsCl, CsBr and ClI, however, set at room temperature in the form of body-centred cubics (the β form) for a reason not perfectly understood. (This has, in fact, been the subject of independent investigations.*) The form of the crystals is here assumed to be that determined by observation. The corresponding formula to (5.01) is deduced from equation (3.06) to be

$$(4.070) e^2 a^{n_{12}-2} = 2\lambda_{12} \left[\frac{2^{n-1}}{3^{(n-1)/2}} B_{n-1} - A_{n-1} \right] \\ + \lambda_{11} A_{n_{11}-1} a^{n_{12}-n_{11}} + \lambda_{22} A_{n_{22}-1} a^{n_{12}-n_{22}}. \quad (5.02)$$

Using the force constants given in Tables II, III, IX and X, we find the following values for the crystal constants:—

Table XI.—Calculated and Observed Interatomic Distances in Crystals.†

$a \cdot 10^8$.	F.		Cl.		Br.		I.	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Na	2.30	2.31	2.85	2.81	2.99	2.97	3.19	3.23
K	2.63	2.66 ₅	3.13	3.14	3.24	3.28 ₅	3.47	3.52 ₅
Rb	3.37*	3.66	3.24	3.27	3.43	3.42	3.58	3.65 ₅
Cs	2.97	3.00	4.21*	$\begin{Bmatrix} 4.12 \\ 4.30 \end{Bmatrix}$	4.34*	4.29	4.56*	4.55 ₈

* Crystals of the β form.

In the same way, the formula (2.06) can be used to calculate the compressibilities of all these crystals. The values of a used in the formula are the calculated values given in the above table, for, in obtaining the expression for the compressibility κ , the relation $\partial\phi/\partial a = 0$ is used, and this is the equation to determine a . This procedure is therefore the logical one to take, and the values of the compressibility obtained are the direct consequence of the force

* O. Emersleben, 'Diss. Göttingen' (1922); Brody, 'Verh. d. Deut. Phys. Gesell.', vol. 24, p. 96 (1922).

† The observed values are taken from W. H. and W. L. Bragg, 'X-rays and Crystal Structure,' p. 306 (1924); cf. also Ch. Manguin, 'La Structure des Cristaux,' p. 224 (1924). The unusual difference between calculated and measured values for RbF is surprising. The experimental value is that of Davey ('Phys. Rev.' (2), vol. 21, p. 149 (1923)). It is to be noted that Spangenberg ('Zs. f. Kristall.,' vol. 57, Heft 5 (1923)), estimates the density of RbF to be 3.740, from which it follows that unit cube = 3.49 Å; by another method he estimates the distance between Rb and F ions to be 2.846, leading to a value of 3.28 Å for the unit cube.

constants given in this paper without any other assumptions. For the body-centred cubics equation (2.06) is used.

Table XII.—Calculated and Observed Compressibilities of Crystals.

$\kappa \cdot 10^{12}$.	F.			Cl.			Br.			I.		
	Calc.	Obs. ¹	Obs. ²	Calc.	Obs. ¹	Obs. ²	Calc.	Obs. ¹	Obs. ²	Calc.	Obs. ¹	Obs. ²
Na	1.40	—	—	3.88	4.20	4.3	4.51	5.08	5.3	5.18	—	7.1
K	2.73	—	—	6.23	5.63	5.2	7.92	6.70	6.4	8.17	8.54	8.8
Rb	3.10	—	—	8.10	—	7.3	7.72	7.94	8.2	9.26	9.58	9.3
Cs	4.90	—	—	7.71	—	5.9	8.58	—	7.0	9.31	—	9.3

The observations in the second column are those of Slater,* and those in the third column those of Richards and Saerens.† A high degree of accuracy in the calculated values cannot be expected, as the value of κ depends very closely on that of n_{12} ; in fact, very approximately $\kappa (n_{12}-2)$ is constant, and so integral values of n_{12} cannot give κ exactly. A change in n_{12} from 9 to 10 decreases κ by about 12 per cent. The agreement between theory and experiment may therefore be regarded as satisfactory on the whole.

A further application of the force constants can be made to calculate the *crystal energies*; that is, the work required to separate to infinity all the ions contained in one gram molecule of the salt. In terms of ϕ , the potential of one ion due to all the rest is given by

$$U = -\frac{N}{2} \phi \text{ in mechanical units,}$$

$$= -\frac{N}{2J} \phi \text{ in thermal units,}$$

whence we obtain for the face-centred cubic

$$U = \frac{N}{2J} \left\{ \frac{(3.495)e^2 z^2}{a} - \frac{\lambda_{11} A''_{n_{11}-1}}{(n_{11}-1) a^{n_{11}-1}} - \frac{\lambda_{22} A''_{n_{22}-1}}{(n_{22}-1) a^{n_{22}-1}} - \frac{2\lambda_{12} A'_{n_{12}-1}}{(n_{12}-1) a^{n_{12}-1}} \right\},$$

and for the body-centred cubic

$$U = \frac{N}{J} \left\{ \frac{(2.035)e^2}{a} - \frac{\lambda_{n_{11}} A_{n_{11}-1}}{2 (n_{11}-1) a^{n_{11}-1}} - \frac{\lambda_{n_{22}} A_{n_{22}-1}}{2 (n_{22}-1) a^{n_{22}-1}} \right. \\ \left. - \frac{\lambda_{n_{12}}}{(n_{12}-1) a^{n_{12}-1}} \left(\frac{2^{n-1}}{3^{(n-1)/2}} B_{n-1} - A_{n-1} \right) \right\}.$$

* Slater, 'Phys. Rev.' (2), vol. 23, p. 488 (1924).

† Richards and Saerens, 'Journ. Amer. Chem. Soc.', vol. 46, p. 934 (1924).

The calculated values, given in Table XIII, may be compared with the "observed" values deduced by Born* from observed heats of formation and other chemical qualities by means of the Born-cycle.

Table XIII.—Calculated and Observed Crystal Energies (in kilo-cals.).

	F.		Cl.		Br.		I.	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Na	226	—	179	183	172	170	163	159
K	195	—	161	165	156	154	148	144
Rb	177	—	156	161	150	151	143	141
Cs	175	—	142	—	138	—	132	—

Similar calculations are possible for the divalent salts, but the observational material available is very much scantier. There are, for instance, no observations of their compressibilities, nor are there any figures available for the crystal energies. The interatomic distances of 16 of these crystals have been calculated, but only about one-half of this number have been measured by X-rays. The dimensions of a few others can be deduced from density measurements. Values obtained in this way are included in brackets in the table (Table XIV).

Of these crystals, the distance of MgO seems to be known with greatest accuracy. Several observers agree in placing it between 2.09 and 2.11 Å.† That of CaO is given as 2.37 and 2.42.‡ The oxides of strontium and barium have been examined by Gerlach,§ with the results given in the Table, but these differ considerably from those determined from density measurements. The selenides of calcium, strontium and barium have been dealt with by Davey,|| and that of strontium also by Slattery.¶

* Born, *loc. cit.*, p. 748.

† Hull, 'Proc. Am. Inst. Elect. Engin.' vol. 38, p. 1171 (1919); Davey and Hoffman, 'Phys. Rev.' vol. 15, p. 333 (1920); Gerlach, 'Zs. f. Phys.' vol. 7, p. 116 (1921); Schiebold, 'Zs. f. Krys.' vol. 56, p. 430 (1921); Hedwall, 'Zs. f. an. Chem.' vol. 120, p. 327 (1922); 'Arkiv Kemi Mineral. Geol.' vol. 8, No. 11; Wychoff, 'Am. J. Sci.' vol. 138 (1921); cf. also Ch. Manquin, 'La Structure des Cristaux,' p. 226 (1924); and W. H. and W. L. Bragg, 'X-rays and Crystal Structure,' 2nd edn., pp. 166 and 304 (1924).

‡ Davey and Hoffman, *loc. cit.*; Gerlach, 'Phys. Zs.' vol. 22, p. 557 (1921); 'Zs. f. Phys.' vol. 9, p. 184 (1922); Davey, 'Phys. Rev.' (2), vol. 21, p. 213 (1923).

§ Gerlach, *loc. cit.*

|| Davey, 'Phys. Rev.' (2), vol. 21, p. 213 (1923).

¶ Slattery, 'Phys. Rev.' (2), vol. 20, p. 84 (1922).

Table XIV.—Calculated and Observed Crystal Distances.

	O.		S.		Se.		Te.	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Mg	2·10	2·09–2·11	2·60	(2·54)	2·61	—	2·69	—
Ca	2·32	2·37–2·42	2·78	2·77	2·76	2·96	2·88	—
Sr	2·45	2·55 (2·63)	2·86	(2·99)	2·96	3·10	2·97	—
Ba	2·63	2·75 (2·81)	3·09	3·20	3·05	3·31	3·14	—

The agreement between theoretical and observed values is not so good as in the case of the crystals of monovalent ions considered above. The discrepancies are greatest in the case of the selenides, and these suggest that possibly the ionic refractivity attributed to Se^{--} is too low. A larger value would result in a larger repulsive force constant, and hence a greater calculated value for all the selenides.

The detailed knowledge of atomic and ionic forces, obtained in this paper, lends itself to further interesting and important applications, such as the calculation of the sizes and heats of formation of complex molecules, and many other physical and thermochemical quantities. It should be of value in theoretical calculations of other crystals more complicated than those considered here, as in the carbonates, for instance. Some of these applications are already being considered.

The Crystal Structure of Barytes, Celestine and Anglesite.

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1. Barytes, BaSO_4 , Celestine, SrSO_4 , and Anglesite, PbSO_4 , crystallise in the di-digonal equatorial class of the orthorhombic system, and are members of a very interesting isomorphous series,* which includes, among other substances, the selenates and chromates of strontium and barium, the perchlorates and permanganates of potassium, rubidium and ammonium, and potassium fluoborate, KBF_4 . Although these compounds belong to several chemically very dissimilar classes, they are all of the type XRO_4 , where X is a kation and RO_4 an anion, and there can be little doubt that, when they crystallise, the size and shape of the RO_4 ion, which is probably very much the same whatever the nature of R, determines the arrangement of the atoms.

This paper describes an attempt to analyse the structures of three crystals of this series. The structures of such crystals must be determined by a process of trial and error. Atomic arrangements must be assumed, and then tested by comparing the intensities of the X-ray spectra predicted from them with those actually observed. The crystals are orthorhombic, and therefore, so far as symmetry is concerned, the atoms have considerable freedom of position. The process of selecting the right structure will be simplified if we can get any idea as to the nature of the SO_4 group. The most reasonable assumption we can make is that the centres of the oxygen atoms lie at the corners of a regular tetrahedron with the sulphur atoms at its centre. The work of Bradley† on the structure of LiKSO_4 shows that this assumption is well founded: the ion in this crystal certainly has a trigonal axis and cannot depart greatly from the regular tetrahedral form, with the distance S to O about 1.5 Å. If we suppose the ion has the same shape and size in other sulphates, we have to deal only with the orientation of the group, considered as a whole, and with the position of its centre. A number of types of arrangement quite consistent with the symmetry of the crystals are thus excluded, and the choice of arrangements to be tested by comparing the observed and

* T. V. Barker, 'Zeitschr. f. Krist.,' vol. 45, Pt. I (1908); Rinne, 'Centralblatt f. Min.,' p. 161 (1924).

† A. J. Bradley, 'Phil. Mag.,' vol. 49, p. 1225 (1925).

calculated intensities is much narrowed down. This method has been followed in the present work, and it has been found possible to assign structures to the three crystals investigated which are practically identical, and which account completely for the observed intensities of the X-ray spectra given by them.

Barytes, celestine and anglesite occur naturally as large well-developed crystals which are very suitable for work with the X-ray spectrometer, since it is possible to compare easily the intensities of the spectra from the different faces. Moreover, the variations in the intensities of a given set of spectra, when one metal is substituted for another in a structure which otherwise probably remains almost unchanged, are of great value in determining the atomic arrangement. The authors have already published a preliminary note on the structure of barytes,* in which the positions of the barium atoms were determined with some degree of accuracy. Considerable doubt remained, however, as to the positions of the SO_4 groups. In the present paper, a more complete study of all three crystals is described, which, while leaving unchanged the positions assigned to the metal and sulphur atoms, has modified considerably those suggested provisionally for the oxygen atoms.

2. The structure of all three crystals appears to be essentially similar. The determination of that of BaSO_4 alone will be described in detail, although data obtained from the other crystals will be employed from time to time.

The axial ratios of BaSO_4 are given by von Groth as

$$a : b : c = 0.8152 : 1 : 1.3136.$$

The specific gravity is 4.49. Referred to these axial ratios, the forms which usually develop are $\{001\}$, $\{110\}$, each very good cleavages, $\{102\}$, $\{011\}$ and $\{104\}$. Other faces required for the X-ray examination were ground on the crystals with emery. The measured spacings of the pinakoid planes are (100) , $4.43 \text{ \AA}$; (010) , $2.72 \text{ \AA}$; (001) , $3.57 \text{ \AA}$; but examination of other planes shows that the structure is based on a simple orthorhombic space-lattice whose unit cell has dimensions

$$a = 8.85 \text{ \AA}, \quad b = 5.43 \text{ \AA}, \quad c = 7.13 \text{ \AA}.$$

For purposes of calculation it is better, therefore, to use the true axial ratio

$$1.6304 : 1 : 1.3136,$$

and this has been employed throughout the paper. Referred to this ratio, von Groth's (h, k, l) becomes $(2h, k, l)$.

From the specific gravity and molecular weight of the crystal we find the unit parallelepiped abc contains four molecules of BaSO_4 .

* 'Manchester Memoirs,' vol. 69, No. 5, p. 1 (1924-25).

3. The first step in determining the structure is to find to which of the 28 space groups possible to its crystal class the barytes arrangement belongs. The possible groups are V_h^1 to V_h^{28} in the notation of Schoenflies.

Referred to the spacings of the unit cell given above, the spacings of the important planes are as follows:—

(100) halved	(111) normal
(010) halved	(101) normal
(001) halved	(201) normal
(110) halved	(102) normal
(210) normal	(011) normal

Using tables such as those given by Wyckoff* or Niggli,† of the co-ordinates of typical points for the different space-groups, we are able to eliminate all space-groups but V_h^{16} . In order to be quite certain that the correct space-lattice was used as the basis of the above determination, it would have been desirable to examine more planes of the type (h, k, l) . During the course of this work, however, papers have appeared by Rinne, Hentschel and Schiebold,‡ and Wyckoff and Merwin,§ on the determination of the space-group of barytes. In both cases the structure is assigned to V_h^{16} , in agreement with the present work, and we may take the space-group of this crystal as definitely known and proceed to the question of fixing the positions of the atoms.

The symmetry planes parallel to (010) are reflexion planes; those parallel to (001) and (100) are glide planes, with glides $a/2$ and $b/2 + c/2$ respectively. The projection of a unit cell on the plane (010) is shown in fig. 1. The plane of the paper is a reflexion plane; other reflexion planes lie $b/2$ above and below it. The dotted lines show the traces of the glide planes (100) and (001). Digonal screw axes (010), perpendicular to the plane of the paper, pass through the centre, corners and mid points of the edges of the cell shown. Centres of symmetry lie on these axes, midway between the reflexion symmetry planes. For the full symmetry elements of the group reference may be made to one of the sources quoted.

4. From symmetry considerations alone we can get a certain amount of information about the distribution of the atoms in the structure. Suppose an atom, A in fig. 1, to lie on one of the symmetry planes (010). By the action of the symmetry elements of the group this atom is multiplied to four at the

* Wyckoff, 'Theory of Space Groups.'

† Niggli, 'Geometrische Cristallographie des Discontinuums.'

‡ 'Zeitschr. f. Krist.,' p. 164 (1925).

§ 'Zeitschr. f. Krist.,' p. 453 (1925).

positions A, B, C and D, all lying within the unit cell. A and B lie on one reflexion plane, C and D on another, $b/2$ above or below. Had the

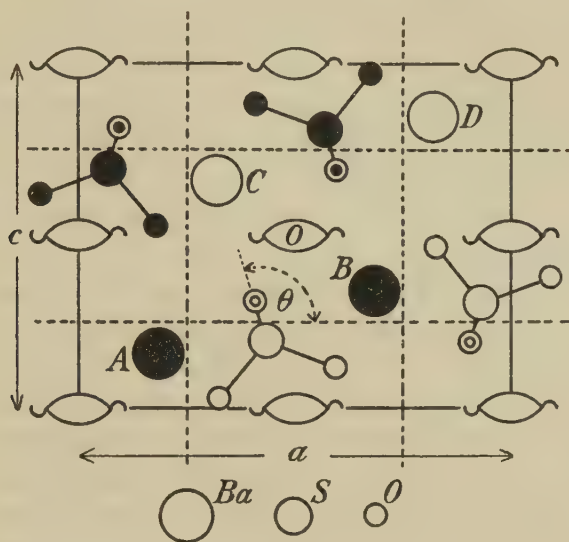


FIG. 1.

atom A been at a point not on a symmetry plane, it would have been multiplied by the operations of the group to eight, unless it had also been at one of the centres of symmetry. There are eight such centres in the unit of structure, but they are of two kinds, and an atom placed at any one of them is multiplied by the operations of the group into four. Now there are only four Ba and four S atoms in the unit of structure, so that we have the following possible types of arrangement for them.

(a) The Ba atoms lie at the symmetry centres of one kind, the S atoms at those of the other.

(b) The Ba atoms lie at symmetry centres, the S atoms on the (010) reflexion planes.

(c) The S atoms lie at symmetry centres, and the Ba atoms on the symmetry planes.

(d) Both Ba and S lie on the (010) symmetry planes as in fig. 1.

An inspection of the intensities of the spectra eliminates the arrangements (a), (b) and (c) at once. In arrangement (a) Ba and S will always be in phase for the spectra from the pinakoid faces. All these faces should give very similar spectra, all of which should be fairly strong. Actually the three sets of spectra are entirely different, and some are very weak. In arrangements (b) and (c)

the planes parallel to (010), containing Ba, lie half-way between those containing S, which would cause much weaker (020) and (060) spectra than are actually observed, as will be explained in a later section. We are therefore left with arrangement (*d*) in which both Ba and S lie on the (010) reflexion planes. Two parameters, x and z , fix one of the barium atoms, and another pair, x' and z' , the sulphur. Once x, z, x', z' are known, symmetry fixes all the Ba and S atoms, but, so far as symmetry considerations alone are concerned, the parameters may have any value.

There are 16 oxygen atoms in each unit, and this permits several different types of arrangement.

(*e*) Let none of the atoms lie on symmetry planes. Any one atom is fixed by three parameters u, v, w , and by the operations of symmetry this multiplies into eight atoms. There may, therefore, be a second independent atom, fixed by u', v', w' , and the total number of oxygen parameters is six.

(*f*) Let half the atoms lie on the reflexion planes and half off them. The eight off the plane are fixed by parameters (u, v, w), the two sets of four on them by u', w' and u'', w'' —giving a total of seven oxygen parameters.

(*g*) Let all the oxygen atoms lie on the reflexion planes. So far as symmetry is concerned there are now four sets of four atoms, each fixed by two parameters, and the total is eight. For the sake of completeness, we must add the following possible arrangements of oxygen atoms, although they are physically very improbable ones.

(*h*) Eight of the sixteen oxygens in the unit may lie at symmetry centres and eight at points not on the symmetry planes, giving three parameters.

(*k*) Eight at the symmetry centres, and two sets of four on the symmetry planes: four parameters.

(*l*) Four at symmetry centres, eight more off the symmetry planes, and four on them: five parameters.

(*m*) Four at symmetry centres, and three sets of four on the symmetry planes: six parameters.

Thus, taking the barium and sulphur into consideration as well, a complete determination of the structure from first principles would require, in the least favourable case, 12 independent parameters to be fixed.

These parameters can only be fixed by considering the intensities of the spectra from the different planes, and, at the present time, our knowledge of the conditions governing the intensity of X-ray reflexion from different atoms and groups is insufficient for an attack on this problem, in its most general form, to be capable of yielding useful results. But, as we have seen, we are

able to make certain assumptions as to the form of the SO_4 group, which simplify matters considerably. It is highly probable that the SO_4 group consists of four oxygen ions strongly attracted to a central sulphur ion with a charge of $+6$.* Such a group, if isolated, would assume a form in which the centres of the oxygen ions lay at the corners of a regular tetrahedron with the sulphur ion at its centre. In a crystal, we might expect the groups to be deformed to a certain extent by the unequal attractions in different directions of the surrounding groups, but the attraction of the oxygen ions to the highly charged sulphur would be much greater than the deforming forces, so that, as a working hypothesis, we are probably justified in treating the SO_4 group as a regular tetrahedral arrangement of oxygen ions around a central sulphur ion.

Bradley† has recently determined the structure of LiKSO_4 . This crystal possesses a trigonal axis, and symmetry considerations show that the SO_4 group must also possess such an axis. This is consistent with a tetrahedral SO_4 ion and, in fact, Bradley finds that a regular tetrahedron with a distance S to O of $1.5 \text{ \AA}$ fits the observed spectra well. The *Reststrahlen*‡ from LiKSO_4 indicate that the SO_4 group has trigonal symmetry, while those from celestine indicate that here the symmetry of SO_4 is no higher than that of the point group V. The *Reststrahlen* are governed by forces brought into play when small displacements of the ions take place; we may expect these forces to be unsymmetrical, even though the group does not depart from the regular tetrahedral arrangement to any appreciable extent. Finally, the very small double refraction of all sulphates may be taken as a further indication of such an arrangement.

5. Assuming the tetrahedral arrangement of the SO_4 group, and remembering that the S ion must lie on a reflexion plane of symmetry, we see that such a plane must also be a plane of symmetry of the group. Two of the oxygen ions will lie in the reflexion plane and two at equal distances on either side of it, and, once the sulphur ion is fixed, two more parameters suffice to fix the group, the distance ρ between the sulphur and oxygen centres and an angular co-ordinate θ (fig. 1) expressing the orientation of the group in the reflexion plane. The total number of parameters to be determined thus reduces to six.

6. To determine these parameters it is necessary to take into account the

* Kossel's assumption has been made here, but it should be pointed out that, had it been assumed that the sulphur and oxygen atoms were bound together by some form of electron sharing, no essential difference either in the argument or in the positions assigned to the atoms would have resulted.

† *Loc. cit.*

‡ C. J. Brester, 'Kristallsymmetrie u. Reststrahlen,' p. 125, Utrecht Dissertations.

intensities of the various spectra. The intensities are measured in the ordinary way by rotating the crystal with uniform angular velocity ω through the range of angles over which it reflects, and measuring E , the total ionization received by the chamber during the rotation. If I is the ionization received by the chamber in the same time, if the direct beam is allowed to enter it, the quantity $E\omega/I$, which is called the "integrated reflexion" and is denoted by R , is a measure of the reflecting power of the face. In every case the crystal face used was large enough for the whole incident beam to fall on it, and all intensities were expressed in terms of a standard, the (400)* reflexion from rock-salt, so that the intensities from one face may be compared with those from another. The angle at which a given spectrum occurs depends only on the spacing of the series of planes from which reflexion takes place, the intensity of the reflexion on the distribution of the diffracting material in each repetition. Suppose in each repetition all the atomic centres are concentrated on a single plane. For any given spectrum, for which the glancing angle is θ , the contributions from the different atoms will all be in phase, and the intensity of the spectrum is the maximum which could occur at that angle, and may be called the normal intensity R_n . If the atoms, considered as diffracting units, are spherically symmetrical, R_n for a given crystal will be a function of θ , the glancing angle of reflexion, and we may write

$$R_n = kf(\theta), \quad (1)$$

where $f(\theta)$ decreases rapidly as θ increases. If the atomic planes are not normal, which is the case for every set of planes in BaSO_4 , the intensity will be less than normal. If R is the intensity for a given spectrum, the ratio R/R_n is known as the "intensity ratio" for that reflexion. The intensity ratio depends on the arrangement of the planes in the repeat of the pattern, and hence on the structure of the crystal. For a given structure, with certain assumptions, the intensity ratios for the different planes can be calculated. Suppose the correctness of an assumed structure is to be tested. Let all the spectra be arranged in order of increasing glancing angle, and let each observed intensity R be divided by the calculated intensity ratio, thus giving R_n . If the structure assumed is the true one, the value of R_n so calculated will die away rapidly and steadily with increasing θ without any violent oscillations in value.† The theoretical difficulty in this process lies in the calculation of the intensity ratio.

* The index (400) is referred to the full spacing of the NaCl lattice; the spectrum is the second order which actually occurs.

† W. L. Bragg, 'Proc. Roy. Soc.,' A, vol. 105, p. 16 (1924).

7. It is usual to treat each atom as a diffracting point, to calculate the resultant amplitude diffracted in any given direction, and to assume that the resultant intensity is the square of the amplitude. Assuming for the moment that this process is valid, a difficulty arises in assigning the appropriate scattering power to a given atom. It has been usual to take the scattering power as proportional to the atomic number—or rather, to the number of electrons in the atom or ion. This would only be correct if all the electrons lay at distances from the atomic centre small compared with the wave-length of the X-rays employed. This is not the case, and we must write for the scattering power of an atom a quantity F , where

$$F = Z\phi(\theta), \quad (2)$$

Z being the total number of electrons in the atom or ion, and $\phi(\theta)$ a function of the glancing angle depending on the distribution of electrons in the atom, which is the unity when $\theta = 0$ and decreases in general as θ increases. This function will be different for each atom, and thus the ratio of the scattering power of two different atoms will itself be a function of θ , which introduces considerable complications for crystals containing several different kinds of atom. For example, we may be sure that the diffracting power of an oxygen ion falls off much more rapidly than that of a barium ion, owing to the fact that the high nuclear charge of the latter will cause a much greater concentration of electrons near the centre of the atom, and we should expect that for high values of θ , the intensities are very little influenced by the oxygen ions and almost entirely due to barium and sulphur; there remains, however, the difficulty of getting numerical values of F for the different atoms.

Mr. D. R. Hartree* has been able to obtain an estimate of the dimensions of the electronic orbits in a number of ions from the consideration of spectral terms. He had already compared the values of F for Na and Cl calculated from his orbits with those obtained experimentally from measurements on rock-salt,† and had found a general agreement, although the measured F fell off more rapidly with θ than the calculated. He kindly undertook to calculate F curves for a variety of ions and his results have recently been published,‡ but we are much indebted to him for supplying us with the necessary figures previous to publication. The values of F used in this work are all based on Hartree's curves, although a few modifications have been introduced which

* 'Proc. Camb. Phil. Soc.,' vol. 21, p. 625 (1923).

† W. L. Bragg, James and Bosanquet, 'Phil. Mag.,' vol. 41, p. 309; vol. 42, p. 1 (1921); vol. 43, p. 433 (1922).

‡ 'Phil. Mag.,' vol. 50, p. 289 (1925).

will be described later. Some of the assumptions on which the calculations of F are based may, perhaps, not be very certain, but there can be little doubt that Hartree's curves represent the general type of diffraction curve of an atom fairly well, and that we shall get nearer to the truth by employing even approximate values than by making no allowance for the effect at all.

8. Suppose now there are n atoms in the unit of structure, and let $F_1, F_2, \dots F_n$ be the diffracting powers of the atoms for the angle corresponding to the m th order spectrum. Let x_n, y_n, z_n be the co-ordinates of the n th atom referred to a centre of symmetry as origin, and expressed as fractions of the lengths a, b, c , of the sides of the unit cell. We shall denote by S the ratio of the amplitude contributed by these atoms to the m th order spectrum from the plane (h, k, l) to that which would have been contributed had the planes been normal. On the ordinary diffraction theory we have

$$S = \frac{\sum F_n \cos 2\pi m (hx_n + ky_n + lz_n)}{\sum F_n}. \quad (4)$$

In what follows we shall calculate S from this formula and assume that the intensity ratio R/R_n is equal to S^2 . Doubt has been thrown by Ewald* on the validity of this procedure, but reasons which appear to justify it will be given in a later section.† In carrying out the calculations we have assumed Hartree's curves for Ba, and Sr, while that for Pb has been estimated from his figures for thallium. The metal has been supposed ionised in each case. We have also assumed the oxygen and sulphur to be ionised and to be O^{-2} and S^{+6} respectively. But we have not applied Hartree's curves directly to these ions. It appears practically impossible to get agreement between observed and calculated spectra for the higher orders, unless O^{-2} is made to die away more rapidly with θ than Hartree assumes. Bradley found the same thing in the case of $LiKSO_4$, and it may possibly be due to the heat motion of the molecules, which would perhaps be more important for the lighter ions. In addition to this, we have tried to make some allowance for the fact that the O ions must be strongly polarized by the S^{+6} ion. This might as a first approximation be regarded as equivalent to increasing the number of electrons surrounding the sulphur. We have taken 16 as the number for $O = 0$ and based the F curve on Hartree's curve for S^{+6} . The difference between the curve so obtained and that for S^{-2} becomes inappreciable for the higher orders. For $\theta = 0$ oxygen must now be taken as 8.5. This procedure appears to be, and is, somewhat arbitrary. It

* Ewald, 'Phys. Zeitsch.,' vol. 26, pp. 29-32 (1925).

† See also W. L. Bragg, 'Phil. Mag.,' vol. 50, p. 306 (1925).

merely represents an attempt to allow for some of the effects which must occur in complex groups of this kind.

Table I.

Sin θ	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70
Ba	54.0	52.6	49.1	44.8	40.7	37.4	34.8	32.5	29.9	27.4	24.6	23.1	21.9	21.1	20.4
Sr	36.0	35.2	33.2	30.6	27.8	25.5	23.8	22.6	21.8	20.6	19.3	17.7	16.0	14.4	13.1
Pb	80	78.5	76.1	72.6	68.5	63.4	58.8	54.4	50.3	46.8	43.7	40.9	38.8	37.0	34.7
S	16	15.2	13.1	10.6	9.3	8.8	8.5	8.1	7.5	6.9	6.3	5.7	5.1	4.6	4.1
O	8.5	8.0	7.2	5.7	4.1	2.5	1.0	—	—	—	—	—	—	—	—

In Table I are given the values of F used, for different values of $\sin \theta$, for the $K\alpha$ radiation of molybdenum, which was employed in these experiments.

9. Column 4 in Tables II, III, and IV give the observed values of the intensity R , for a number of spectra from $BaSO_4$, $SrSO_4$ and $PbSO_4$ respectively. The spectra are arranged in order of increasing glancing angle, and are expressed in absolute measure. The measurements are made in terms of (400) rock-salt, for which the absolute intensity R may be taken as 10^{-4} to a close enough degree of approximation for this work.* The intensities for $PbSO_4$ and $SrSO_4$ are weaker on the whole than those for $BaSO_4$, owing to the fact that each of these substances has a higher absorption coefficient for Mo radiation than $BaSO_4$. The high absorption of $SrSO_4$ is due to the fact that the wave-length of Mo $K\alpha$, $0.7096 \text{ \AA}$, is just shorter than the critical absorption wave-length of Sr, $0.767 \text{ \AA}$, so that the radiation is abnormally absorbed, and is therefore unsuitable for investigating crystals containing strontium. If allowance is made for the different absorptions, it will be seen that the general run of intensities is very similar for all three crystals. Some of the principal spectra from $BaSO_4$ are plotted in fig. 2; the ordinates give values of R , the abscissæ $\sin \theta$. It will be seen that the spectra from (010) are on the whole stronger than those from the other faces, and that they decrease steadily in intensity with increasing order. This is to be expected, for we have seen that symmetry requires Ba, S, and two O ions to lie on the (010) planes, which are symmetry planes. These planes are, in fact, nearly normal, with a spacing half that of the b spacing of the unit cell, so that all the odd orders are absent and only (020), (040), (060) and so on occur. Assuming the SO_4 group to have the regular tetrahedral arrangement, and taking the radius sulphur to oxygen as $1.5 \text{ \AA}$, it is easy to calculate the amplitude factors for these spectra, and so to calculate the normal intensities. The calculated normal curve is shown in

* $F\omega/I$ for Mo $K\alpha$ (200)/NaCl = 4.8×10^{-4} and (200) : (400) = 5 : 1, approximately.

fig. 2 (curve A), and is of great value, for from it we can now estimate the ratio S for each spectrum to which the ratio calculated from any assumed arrangement of atoms must correspond if the structure is correct.

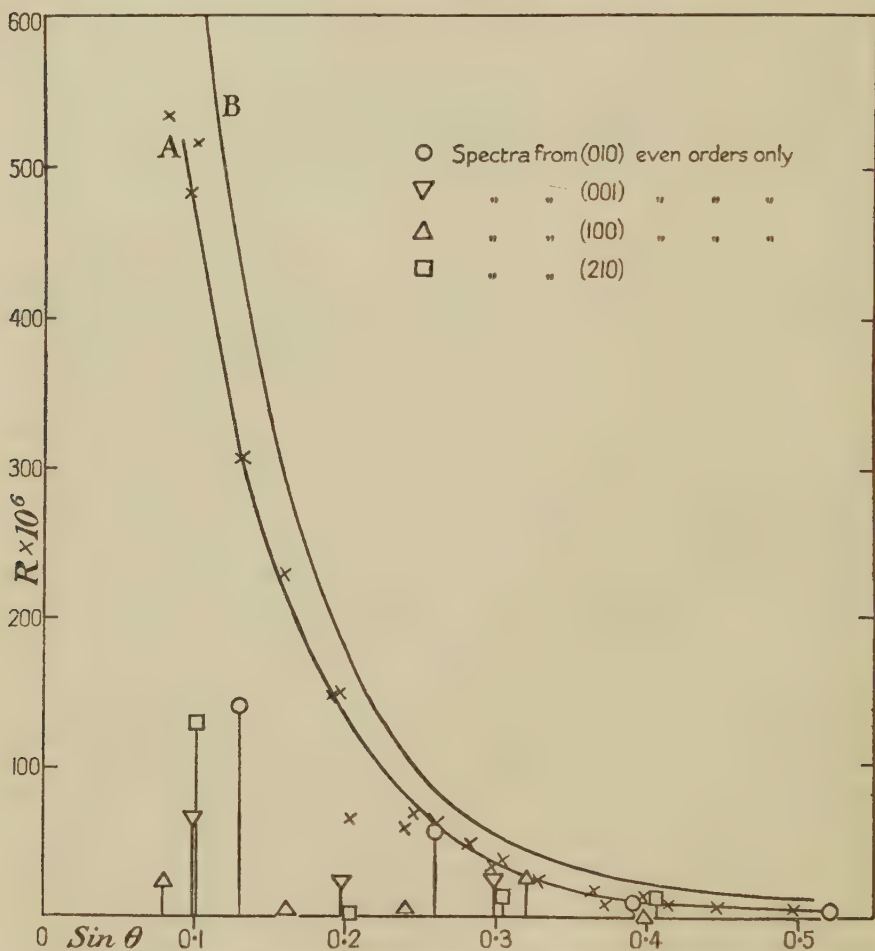


FIG. 2.—The crosses represent the values of R/S^2 calculated from the structure.

In the case of BaSO_4 and PbSO_4 the intensities of the higher orders of spectra will be almost entirely governed by the positions of the metal ions, and even the lower orders very largely influenced by them. The first step is then to obtain the approximate positions of these ions. The Ba and S can only move in the (010) planes; each have, therefore, an x and z parameter to be determined. The (100) and (210) spectra are affected by the x parameter only, and (011) and (001) by the z only, and an examination of these four spectra suffices to fix approximately the position of Ba and S.

Table II.—BaSO₄.

Spectrum.	Glancing Angle θ .	Sin θ .	$\frac{E\omega}{I} \times 10^6$ = $R \times 10^6$.	S.	S ² .	$\frac{R}{S^2} \times 10^6$.	Calculated Values of R_n .
101	3 40	0.0639	—	0.04	0.0016	—	—
200	4 35	0.0799	23.5	0.21	0.044	533	850
011	4 43	0.0822	31.0	0.219	0.048	642	840
201	5 24	0.0941	12.0	0.135	0.018	653	755
002	5 42	0.0993	67.4	0.375	0.141	477	720
210	5 50	0.1016	130	0.502	0.252	517	695
202	7 20	0.1276	—	0.000	0.000	—	—
020	7 29	0.1302	140	0.678	0.458	306	435
400	9 13	0.1602	6.2	0.163	0.027	232	290
022	9 27	0.1642	6.3	0.134	0.018	350	275
402	10 51	0.1882	—	0.066	0.004	—	—
303	11 3	0.1917	47.3	0.578	0.334	142	195
004	11 26	0.1982	24.4	0.396	0.156	155	182
420	11 45	0.2036	2.7	0.064	0.004	65	170
600	13 54	0.2402	4.6	0.276	0.076	60	106
033	14 16	0.2464	0.42	0.076	0.0058	70	100
404	14 48	0.2554	—	0.033	0.001	—	—
040	15 6	0.2605	52.5	0.974	0.940	56	85
603	16 24	0.2823	0.5	0.100	0.011	47	66
006	17 18	0.2974	24.8	0.875	0.762	32.5	55
630	17 47	0.3054	13.0	0.578	0.335	38	50
505	18 38	0.3195	—	0.30	0.090	—	41
800	18 42	0.3206	26.1	0.975	0.950	27.5	40.8
044	19 10	0.3283	6.7	0.523	0.273	24.5	38
804	22 7	0.3765	4.2	0.453	0.205	20.5	26.7
606	22 33	0.3835	3.0	0.570	0.325	9.2	25.4
060	23 1	0.3910	11.2	1.0	1.0	11.2	24.1
008	23 23	0.3969	2.2	0.367	0.134	15.2	23.0
10, 00	23 27	0.3979	2.0	0.326	0.106	19	22.8
840	24 2	0.4073	13.4	1.0	1.0	13.4	21.2
055	24 14	0.4104	4.8	0.724	0.522	9.2	20.8
10, 05	26 34	0.4472	3.1	0.717	0.507	6.1	16.4
066	29 31	0.4927	3.2	0.880	0.772	4.2	12.0
00, 10	29 44	0.4960	1.7	0.560	0.309	5.5	11.7
10, 50	30 36	0.5090	4.0	0.835	0.698	5.8	10.7
080	31 25	0.5213	3.7	1.0	1.0	3.7	9.9
0, 10, 0	45 39	0.6514	1.4	1.0	1.0	1.4	5.3

Table III.— SrSO_4 .

Spectrum.	θ .	$\sin \theta$.	$R \times 10^6$.	S.	S^2 .	$\frac{R}{S} \times 10^6$.	Calculated values of $R_n \times 10^6$.
101	3 50	0.0669	—	0.024	0.0006	—	—
011	4 49	0.0842	4.52	0.091	0.0083	595	460
200	4 52	0.0849	2.03	0.080	0.0064	320	455
201	5 43	0.0995	trace	0.064	0.004	—	—
002	5 57	0.1037	22.6	0.330	0.109	208	350
210	6 11	0.1077	43.2	0.478	0.228	194	330
020	7 36	0.1323	54.5	0.636	0.404	135	220
202	7 41	0.1339	—	0.057	0.003	—	—
022	9 42	0.1683	1.44	0.136	0.018	77.6	134
400	9 46	0.1697	trace	0.217	0.046	—	—
402	11 29	0.1990	—	0.115	0.010	—	—
303	11 35	0.2008	19.6	0.594	0.352	55.6	89
004	11 58	0.2074	7.7	0.339	0.114	67.2	83
420	12 26	0.2154	—	0.101	0.010	—	—
033	14 37	0.2525	—	0.052	0.003	—	—
600	14 45	0.2546	trace	0.232	0.054	—	—
040	15 21	0.2646	23.4	0.892	0.782	30.0	39
404	15 32	0.2678	—	0.045	0.002	—	—
603	17 22	0.2985	—	0.065	0.004	—	—
006	18 7	0.3111	7.8	0.798	0.635	12.3	23
630	18 51	0.3231	5.1	0.480	0.232	22	18.7
505	19 33	0.3347	—	0.320	0.102	—	—
044	19 40	0.3366	1.5	0.409	0.167	8.8	16.7
800	19 51	0.3395	7.8	0.925	0.855	9.1	16.1
060	23 23	0.3969	3.47	1.00	1.00	3.47	11.2
804	23 27	0.3980	—	0.186	0.035	—	—
606	23 41	0.4016	trace	0.535	0.286	—	—
008	24 31	0.4148	1.6	0.420	0.176	9.1	10
055	24 53	0.4208	1.2	0.664	0.440	2.75	9.8
10, 00	25 7	0.4243	trace	0.091	0.008	—	—
840	25 31	0.4306	4.7	0.930	0.860	5.5	9.1
10, 05	29 50	0.4976	0.24	0.646	0.418	0.5	6.3
080	31 57	0.5292	1.64	1.00	1.00	1.64	5.1
10, 50	32 35	0.5385	1.27	0.962	0.925	1.37	4.8

In terms of the normal intensities, the spectra from (100) are as follows:—Odd orders all absent, showing that the a spacing is halved. Of the even orders (200) is small, (400) small, (800) nearly normal, (10,00) fairly large. Those from (210),* which is not halved, are (210) large, (420) very small, (630) small, (840) normal. The large (800) and small (400) suggest at once that the

* Note that (210) is the crystallographers' (110), an important cleavage plane of the crystal.

Table IV.--PbSO₄.

Spectrum.	θ .	Sin θ .	$R \times 10^6$.	S.	S ² .	$\frac{R}{S^2} \times 10^6$.	Calculated Values of $R_R \times 10^6$.
101	3 47	0.0660	—	0.062	0.004	—	—
200	4 49	0.0839	19.8	0.331	0.109	182	455
201	5 39	0.0983	7.9	0.260	0.067	120	350
002	5 52	0.1022	24.2	0.437	0.191	127	335
210	6 8	0.1069	30.1	0.518	0.268	112	313
020	7 35	0.1318	61.0	0.780	0.608	101	225
202	7 35	0.1320	—	0.131	0.017	—	—
400	9 37	0.1679	trace	0.030	0.009	—	—
303	11 25	0.1979	20.3	0.726	0.526	38.6	109
004	11 47	0.2044	5.7	0.307	0.094	60	103
420	12 21	0.2138	—	0.034	0.001	—	—
600	14 35	0.2518	3.1	0.386	0.149	20.8	62
040	15 17	0.2636	18.3	0.988	0.975	18.5	57
404	15 18	0.2639	—	0.0095	0.0009	—	—
006	17 51	0.3066	8.6	0.902	0.814	10.6	35
630	18 42	0.3207	4.3	0.774	0.597	7.2	19.2
800	19 37	0.3358	8.5	1.00	1.00	8.5	17.2
060	23 17	0.3954	2.7	1.00	1.00	2.7	16.0
606	23 19	0.3958	0.87	0.50	0.25	3.5	15.9
008	24 8	0.4088	1.9	0.824	0.675	2.8	14.7
840	25 19	0.4276	2.31	0.988	0.975	2.4	12.9
00, 10	30 44	0.5110	trace	0.13	0.017	—	8.2
080	31 49	0.5272	0.44	1.00	1.00	0.44	7.3
10, 50	32 19	0.5345	0.44	0.553	0.305	1.43	7.1
0, 10, 0	41 13	0.6590	trace	1.00	1.00	—	4.1

(100) planes containing barium are separated by $\frac{1}{8}$ of the whole a spacing of 8.85 Å, and this is confirmed by the small second and large fourth order from (210). The fact that both (800) and (840) are practically normal means that the sulphur atoms must be helping the barium atoms in these orders, whereas they are nearly out of phase with them in (400) and (420). To decide which of several possible arrangements of sulphur will fulfil these conditions we notice that (210) is large while (200) is small. A projection of an approximate structure, in which only Ba and S are shown on the (001) plane, is shown in fig. 3 (i), and it will be seen that the arrangement there shown explains the difference in the two sets of spectra. For (100), the planes follow in the sequence Ba, Ba, S, S, Ba, Ba, S, S, each separated by $\frac{1}{8}$ of the complete spacing. Thus, Ba and S reinforce in (800), but act against one another in (200). For (210) the sequence of planes is BaS, BaS, separated by $\frac{1}{4}$ of the spacing, followed by a gap of $\frac{3}{4}$ of the spacing, and so on, so that here Ba and S always

help one another. To confirm the hypothesis that the metal and sulphur ions help one another in the 4th orders, we have taken a few spectra from

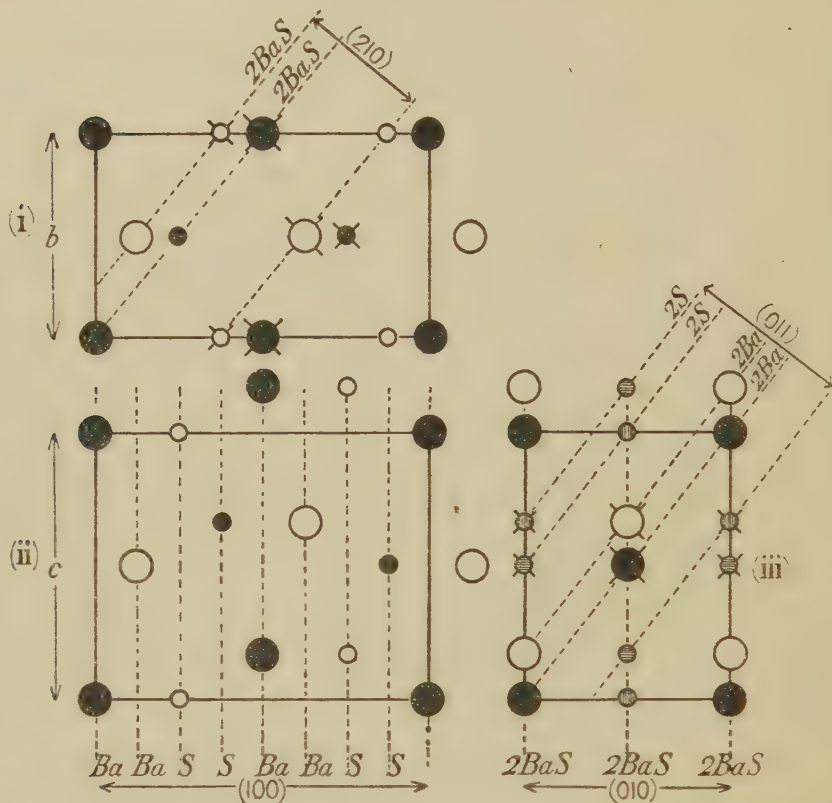


FIG. 3.

Large circles represent Ba atoms, small circles S.

Plain black circles represent atoms in the plane of the paper.

Plain white circles represent atoms in half a unit above or below the black.

Horizontally shaded circles represent atoms $a/4$ below the plane of the paper, vertically shaded, those $3a/4$ below.

Circles with crosses lie $c/6$ above the corresponding plain circles in 3 (i), and $a/8$ above in 3 (iii).

$KMnO_4$, where the heavier Mn replaces the lighter S, and the light K the heavy Ba. Here again we find a large (800) and small (200) and (400), as we should expect from the structure assumed.

To get an approximate idea of the z parameters, we notice that (006) is fairly large, (033) small or absent, (066) large, and (011) comparatively small.

This indicates that the (001) planes containing Ba are separated by about $\frac{1}{6}$ of the complete c spacing, while the small (011) and the larger (001) suggest that the S ions help the Ba ions in the latter, but are out of phase with them in the former. These simple considerations enable us to assign the following provisional co-ordinates to the four Ba and four S ions in the unit of the structure.

Ba.			S.		
$-\frac{5}{16} - x,$	$-\frac{1}{4},$	$-\frac{1}{3} - z,$	$-\frac{1}{16} - x',$	$\frac{1}{4},$	$-\frac{1}{3} - z',$
$\frac{5}{16} + x',$	$\frac{1}{4},$	$\frac{1}{3} + z,$	$\frac{1}{16} + x',$	$-\frac{1}{4},$	$\frac{1}{3} + z',$
$-\frac{3}{16} + x,$	$\frac{1}{4},$	$\frac{1}{6} - z,$	$-\frac{7}{16} + x',$	$-\frac{1}{4},$	$\frac{1}{6} - z',$
$\frac{3}{16} - x,$	$-\frac{1}{4},$	$-\frac{1}{6} + z,$	$\frac{7}{16} - x',$	$\frac{1}{4},$	$-\frac{1}{6} + z',$

Here the co-ordinates are referred to the centre of symmetry (O in fig. 1) as origin, and are given as fractions of the lengths a, b, c , of the sides of the unit cell. The quantities x, x', z, z' are small adjustments to the approximate co-ordinates assumed, which must be determined by a closer comparison of the spectra. As a matter of fact they all turn out to be quite small. The positions of the atoms in fig. 3 are plotted from the above co-ordinates, neglecting the x 's and z 's.

10. The approximate values given above are used to calculate the structure ratio S for the high-order spectra where the effect of the oxygen can be neglected, and from these, the small adjustments x, x', z, z' are determined. Very similar values for the metal and sulphur co-ordinates are found to give good fits in the case of SrSO_4 and PbSO_4 . Assuming now that the positions of Ba and S are known, we turn our attention to the oxygen atoms. So long as we keep to the tetrahedral group, we have to determine only two parameters, the radius of the group, which we have taken as $1.5 \text{ \AA}$, and θ , which expresses the orientation of one of the SO_4 groups in the (010) planes. (The angle θ is shown in fig. 1.) We have been able to get correspondence between the observed and calculated spectra with a group of the type assumed. Possibly a closer agreement could have been obtained by introducing distortions into the SO_4 group, but it is doubtful whether they would have had any physical significance. To determine θ the values of S' were calculated for a series of values of θ from 0° to 360° . Certain ranges of θ were at once ruled out, and much the best fit was given by values in the neighbourhood of $\theta = \pm 100^\circ$. It is not possible to be sure of the best value of θ within a range of from 5° to 10° on either side of the value $\theta = 100^\circ$. The exact value assigned to θ depends on the assump-

tions made as to the form and diffracting power of the SO_4 group. The O atoms contribute a relatively small amount to the total intensity, and we must not base more on the initial assumptions than they can fairly bear. It will be seen later that, physically, there appears to be some reason for preferring a value of 0 in the neighbourhood of 100° , although actually the value was determined independently, entirely from intensity measurements.

Probably in crystals like KClO_4 , or NH_4ClO_4 where the O atoms are relatively much more important as regards their diffracting power, it would be easier to determine their position accurately, but only quite small crystals of these substances have been obtained, and the technical difficulties of making accurate intensity measurements with them are considerable. The values of R/S^2 calculated with this value of θ are shown in column 7, Tables II, III and IV. The values of R/S^2 even now do not fall away quite regularly, but on the whole the agreement for all three substances is good. There is no case where a small structure factor corresponds to a large spectrum, or *vice versa*, and all the spectra which are absent would be predicted as absent, or very small, from their structure factors. Many of the irregular spectra are rather weak, and therefore difficult to measure accurately; several different crystals have been used in each case, which may cause irregularities, due to the different degrees of perfection of the faces, and it must be remembered that we have assumed the atoms to be spherically symmetrical as regards their scattering power. That this will be the case when the ions are combined to form a group such as SO_4 is by no means certain.

11. In calculating the intensity ratio R/R_0 we have assumed it equal to S^2 . This needs some justification, since, according to Ewald,* it should vary as S for a perfect crystal. This, in fact, appears to be true, or nearly so, for diamond,† calcite‡ and aragonite§ which are all very perfect crystals, with small absorption coefficients. The matter has also been considered theoretically by Darwin, and experimentally, in the case of rocksalt, by W. L. Bragg, James and Bosanquet.¶ We may interpret the matter by supposing a largely increased effective absorption coefficient at the reflecting angle, the increase being propor-

* *Loc. cit.*

† W. H. Bragg, 'Proc. Phys. Soc. Lond.,' vol. 33, p. 304 (Aug., 1921).

‡ W. H. Bragg, 'Phil. Trans. Roy. Soc.,' A, vol. 215, p. 253 (1915).

§ W. L. Bragg, 'Roy. Soc. Proc.,' A, vol. 105, p. 16 (1924).

¶ C. G. Darwin, 'Phil. Mag.,' vol. 43, p. 800 (1922).

¶ 'Phil. Mag.,' vol. 42, p. 1 (1921).

tional to the reflecting power of the faces, and being greater the more perfect the crystal. We may then write

$$R \propto \frac{S^2}{\mu + kR} \quad (11.1)$$

where k may be called the extinction coefficient. If kR is large compared with μ , this leads at once to the law $R \propto S$,* but for crystals such as those under investigation, where μ is large, we might expect on this view that $R \propto S^2$ would be more nearly true. It appears desirable, however, to have some numerical confirmation of this assumption. The integrated reflexion R is given by the following expression:—

$$R = \frac{E\omega}{I} = \frac{N^2\lambda^3}{4\mu} \cdot \frac{|e|^4}{m^2c^4} \frac{1 + \cos^2 2\theta}{\sin 2\theta} S^2 e^{-B \sin^2 \theta} \times (\Sigma F)^2. \quad (11.2)$$

Here N is number of molecules per c.c. in the crystal.

λ is wave-length of the radiation employed.

e, m are the charge and mass of an electron.

c is velocity of light.

μ is linear absorption coefficient for wave-length λ , and should include extinction.

The factor $(\Sigma F)^2$ is the square of the sum of the F factors for the atoms in the molecule, and $e^{-B \sin^2 \theta}$ is the Debye factor, which allows for the decrease in intensity due to heat-motion. It will be different for each atom, and probably different for different crystallographic directions, and should not strictly be separated from (ΣF) . If the planes are normal, S is unity, and, using the values for F employed already, we can calculate the numerical values of R_n for a series of glancing angles, neglecting for the time the Debye factors, which are not known for these substances. The absorption coefficients for BaSO_4 , SrSO_4 , and PbSO_4 have not been measured directly, but, from tables of mass absorption coefficients for molybdenum radiation given by Windgårdh† the linear absorption coefficients for the crystal can be calculated. We find in this way for BaSO_4 $\mu = 116$, for SrSO_4 , $\mu = 184$, and for PbSO_4 $\mu = 451$. These are, of course, the ordinary absorption coefficients, unaffected by extinction. Using these values, we obtain *

$$R e^{-B \sin^2 \theta} = \frac{(\Sigma F)^2}{b} \frac{1 + \cos^2 2\theta}{\sin 2\theta}$$

* W. L. Bragg, 'Phil. Mag.,' vol. 50, p. 306 (1925).

† 'Zeitsch. f. Phys.,' vol. 8, p. 363 (1922).

where

$$b = 1.21 \times 10^8 \text{ for BaSO}_4$$

$$b = 1.53 \times 10^8 \text{ for SrSO}_4$$

$$b = 4.02 \times 10^8 \text{ for PbSO}_4.$$

The last column in tables II. III and IV give the values of R_n for the different spectra, calculated from this formula. In fig. (2), curve B, the calculated normal curve for BaSO_4 , uncorrected for the Debye factor, is plotted as well as the normal curve A, estimated from the (010) face. The values of R/S^2 all lie on or near this estimated normal curve, but it will be seen that the calculated values are all much higher than the observed ones. Allowance for the Debye factor will reduce this discrepancy to some extent, particularly for the high orders, for the crystals are all soft, and the Debye factor, therefore, probably considerable, but it will not affect the lower orders very much. These, however, will be more likely to be reduced by extinction. The discrepancies are all in the right direction, and the manner of plotting such as to emphasise them, since the intensities depend on F^2 . The values of R_n calculated in a similar manner, and based on the idea that BaSO_4 is a perfect crystal, which is that considered by Ewald, and which leads to the result that $R \propto S$, are far below those actually observed. BaSO_4 must approximate more to the fine mosaic type of crystal, consisting of small more or less perfect fragments set at slightly differing angles, to which alone, as shown by Darwin,* the formula (11.2) can be applied. It appears from these results that in working out these crystals it is better to assume that the intensity ratio varies as S^2 . The difference between the observed and calculated normal orders is greatest in the case of lead sulphate. This is interesting, because, for equal perfection of crystal, we should expect the extinction effect to be least in the case of lead, owing to the large value of μ . If, however, any layer is produced by grinding, in which the orientation of the particles is quite different from that of the crystal as a whole, it will tend to reduce the intensities of the spectra much more for crystals with a high absorption coefficient, and the reduction will be most for low glancing angles, and should be a function of the glancing angle. It is possible that at least some of the discrepancy is due to this. There remains, however, the possibility that the inner electrons in an atom as heavy as lead do not contribute the full quota to the diffraction to be expected from the simple classical formula. Accurate intensity measurements from a crystal which contains a heavy atom, and whose structure is known, so that

* Darwin, *loc. cit.*

there is not the additional uncertainty of structure factor, would be of great interest in this connection.

12. The co-ordinates of the four typical Ba and four typical S ions have already been given in Section 9. We repeat them here for convenience of reference :—

Ba.			S.		
$-\frac{5}{16} - x,$	$-\frac{1}{4},$	$-\frac{1}{3} - z,$	$-\frac{1}{16} - x',$	$\frac{1}{4},$	$-\frac{1}{3} - z',$
$\frac{5}{16} + x,$	$\frac{1}{4},$	$\frac{1}{3} + z,$	$\frac{1}{16} + x',$	$-\frac{1}{4},$	$\frac{1}{3} + z',$
$-\frac{3}{16} + x,$	$\frac{1}{4},$	$\frac{1}{6} - z,$	$-\frac{7}{16} + x',$	$-\frac{1}{4},$	$\frac{1}{6} - z',$
$\frac{3}{16} - x,$	$-\frac{1}{4},$	$-\frac{1}{6} + z,$	$\frac{7}{16} - x',$	$\frac{1}{4},$	$-\frac{1}{6} + z'.$

The co-ordinates are referred to a centre of symmetry as origin, and are expressed as fractions of the lengths a, b, c of the side of the unit lattice cell. The atoms whose positions are given are those shown in fig. 1. The quantities x, x', z, z' are small variations from the approximate co-ordinates assumed provisionally, which are those shown in fig. 2. These approximate co-ordinates are the same for all three crystals examined, while the values of x, x', z, z' differ slightly from one to the other.

The centres of the oxygen ions form a regular tetrahedron with the sulphur ion at its centre, the radius S to O being $1.5 \text{ \AA}$. The (010) reflexion planes are reflexion symmetry planes of the SO_4 groups whose centres lie in them, and the orientations of the groups in the planes are fixed by an angular co-ordinate θ (see fig. 1). The value $\theta = 100^\circ$ has been used for all three crystals, although it probably differs slightly for each one, and it cannot be fixed with great accuracy, since the intensities of the spectra are not very sensitive to small changes of θ .

The following summary gives the data for the three crystals investigated :—

Barytes : BaSO_4 . Axial ratio, $1.6304 : 1 : 1.3136$.*

$a = 8.85 \text{ \AA}, b = 5.43 \text{ \AA}, c = 7.13 \text{ \AA}.$

$x = 0.0055, x' = 0.0055, z' = 0.0055, z' = -0.028.$

In Ångström units

$ax = 0.049 \text{ \AA}, cz = 0.039 \text{ \AA}, ax' = 0.049 \text{ \AA}, cz' = -0.20 \text{ \AA}$

* No attempt has been made to obtain a more accurate value of the axial ratio from the X-ray data. The crystallographers' values, which are well known for these crystals, have been assumed throughout, but the calculated and observed positions of the spectra agree very closely in all cases.

Celestine : SrSO_4 . Axial ratio, 1.5580 : 1 : 1.2800.

$$\begin{aligned} a &= 8.36 \text{ \AA}, & b &= 5.36 \text{ \AA}, & c &= 6.84 \text{ \AA} \\ x &= 0.0083, & z &= 0.0055, & x' &= -0.0055, & z' &= -0.028 \\ \text{or } ax &= 0.070 \text{ \AA}, & cz &= 0.038 \text{ \AA}, & ax' &= -0.046 \text{ \AA}, & cz' &= -0.19 \text{ \AA}. \end{aligned}$$

Anglesite : PbSO_4 . Axial ratio, 1.5704 : 1 : 1.2894.

$$\begin{aligned} a &= 8.45 \text{ \AA}, & b &= 5.38 \text{ \AA}, & c &= 6.93 \text{ \AA} \\ x &= 0.0028, & z &= 0.0042, & x' &= -0.0055, & z' &= -0.028 \\ \text{or } ax &= 0.024 \text{ \AA}, & cz &= 0.030 \text{ \AA}, & ax' &= -0.046 \text{ \AA}, & cz' &= -0.19 \text{ \AA}. \end{aligned}$$

13. The structure given in Section 12 was obtained entirely from consideration of the intensities of the spectra. It is interesting to see whether any physical reason can be given for it, especially as it appears to be the structure typical of a whole class of compounds. From other work, there is reason to believe that the forces of repulsion between two oxygen ions assume very great values when their centres approach within about $2.7 \text{ \AA}$. In the tetrahedral SO_4 ion assumed, the distance between the oxygen centres is actually only $2.45 \text{ \AA}$, but we may reasonably suppose that the intense attraction of an S^{+6} ion will diminish the distance of approach to some extent. If we describe about each oxygen centre a sphere of $1.35 \text{ \AA}$ radius, the spheres will intersect, but may be considered as defining the boundary of the SO_4 group, within which the other divalent ions in the structure will not be able to penetrate. With the same limitation to the meaning of the term, we may take as the radius of the Ba ion $1.4 \text{ \AA}$, and might therefore be doubtful of the correctness of any structure in which the centres of a Ba ion lay within less than about $2.7 \text{ \AA}$ of an oxygen ion.

In fig. 4 the structure of BaSO_4 is shown diagrammatically, viewed in a direction perpendicular to the (010) face. The circles represent to scale the radii of the ionic domains. The black circles represent barium, the white oxygen, which are combined to form the tetrahedral SO_4 groups. The three Ba ions at the top and the three at the bottom of the diagram lie in one plane, say that of the paper, the remaining three a distance $b/2$ below. The middle row of SO_4 groups have their centres in the plane of the paper, the other $b/2$ below. Consider now the five Ba ions on the left and lower portion of the diagram, together with the two more which lie $b/2$ above the plane of the paper and directly over the middle pair of ions. Into the space between these seven ions the SO_4 group S shown in the diagram fits quite neatly. The two lower O ions touch the two lower barium and the upper barium touches each of the two upper O ions, which lie above and below the plane of the

paper. This "unit" of barium ions containing an SO_4 group is repeated indefinitely throughout the structure according to the symmetry operations

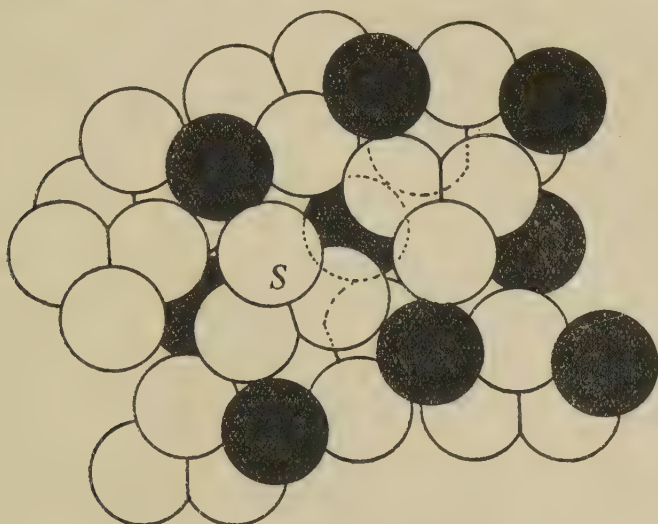


FIG. 4.

of the group. If now we fix on any particular barium ion, and calculate the distance from it of the neighbouring oxygen ions, we find that in this structure 12 O ions lie within a sphere of a little more than $3 \text{ \AA}$ radius described about each Ba ion. The distances are as follows: Two at $2.89 \text{ \AA}$, two at $2.78 \text{ \AA}$, two at $2.82 \text{ \AA}$, two at $3.31 \text{ \AA}$, two at $3.08 \text{ \AA}$, one at $2.80 \text{ \AA}$, and one at $2.71 \text{ \AA}$. Moreover, in the structure assumed, none of the ionic domains of O ions belonging to different SO_4 groups intersect one another. Thus the structure appears to be one in which each positive metallic ion is surrounded as closely and as uniformly as possible by negative oxygen ions, perfect freedom of adjustment of the ions being hampered, because they are attached together in fours in the sulphate groups. The position of a typical barium ion may be understood by considering the middle ion in fig. 4. Five of the SO_4 groups concerned are shown, accounting for eight of the 12 oxygen ions. The remaining groups are those which lie a whole spacing below the right-hand pair in the middle row.

The similarity of structure and axial ratio in crystals isomorphous with barytes would thus be accounted for, for the structure on this view is determined by the tetrahedral arrangement of O ions in the group RO_4 . If the middle ion R is larger we might expect the whole structure to be expanded with but little alteration of the axial ratio. Change in the size of the metallic

ion would no doubt affect the closeness with which the oxygens could pack, and hence the orientation of the groups and the axial ratios, but we should not expect the effect to be very large. A certain number of observations have been made on KMnO_4 and KClO_4 , and these entirely confirm the view that the structures are essentially similar to those of the three sulphates. The main spacings of the five crystals are given below in Table V for comparison.

Table V.—Spacings in Å units.

Crystal.	<i>a.</i>	<i>b.</i>	<i>c.</i>
BaSO_4	8·85	5·43	7·13
SrSO_4	8·36	5·36	6·84
PbSO_4	8·45	5·38	6·93
KClO_4	8·84	5·68	7·22
KMnO_4	9·08	5·70	7·40

Summary.

1. The structures of the isomorphous sulphates of barium, strontium and lead have been investigated, and all are found to be very similar. The structure is based on a simple orthorhombic lattice having four molecules to the unit cell, and the space group is V_h^{16} . The positions of the atoms in the structure have been determined by a study of intensities.

In calculating the structure factors, the figures for the diffracting power of ions at different angles, calculated by Hartree, have been employed with slight modifications. A comparison of the absolute intensity of reflexion actually observed with that calculated on the classical theory has been made. It is found that the observed intensity is in all cases lower than, although of the same order of magnitude as, the calculated.

A possible reason for the structure which is common to a number of crystals is discussed.

In conclusion we wish to express our thanks to Prof. W. L. Bragg, F.R.S., for his constant interest in this work. We are also greatly indebted to Mr. T. V. Barker, of the Crystallography Department at Oxford, for supplying us with specimens of a number of crystals belonging to the isomorphous series under investigation: and to Mr. J. M. Wordie, of St. John's College, Cambridge, who gave us several very fine natural crystals of celestine. The Coolidge bulb used in this work was the gift of the General Electric Company of Schenectady, and part of the apparatus was purchased with the aid of a grant from Messrs. Brunner, Mond, Ltd., to whom our best thanks are due.

*On Some Direct Evidence for Downward Atmospheric Reflection
of Electric Rays.*

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1. *Introduction.*

In a recent paper in these Proceedings (Series A, vol. 107, p. 587) Smith-Rose and Barfield have called attention to the two outstanding problems of the propagation of wireless waves over the earth's surface. A complete theory of wireless transmission must explain (*a*), why long-distance communication is possible, and (*b*), why large and rapid variations of signal intensity and apparent direction of propagation of the waves are observed at night, and, to some extent, during daylight, particularly in winter. Smith-Rose and Barfield further point out that both phenomena can be explained to some extent by the well-known Kennelly-Heaviside layer theory, but that it is generally admitted that further evidence of the existence of the layer is needed. They also describe accurate experiments designed to detect the existence of waves arriving at a wireless receiver in a downward direction (*i.e.*, inclined to the horizontal), such as must be present if the Heaviside layer theory is correct.

In these experiments Smith-Rose and Barfield sought, by directional methods, to detect a departure of the electric field of the waves from the vertical by means of a large Hertzian oscillator, and a departure of the magnetic field from the horizontal by means of a rotating frame aerial. It was, however, found that the conductivity of the ground was sufficiently high to make it act very nearly as a perfect reflector, and, because of the presence of the reflected wave from the ground, none of the effects sought for could be detected even in conditions such as are normally associated with signal strength and directional variations. These authors therefore concluded that the results of their experiments could not be considered as evidence for or against the Heaviside layer theory. In a later paper,* Smith-Rose and Barfield describe further experiments of this type, again with negative results, and state that "adequate experimental evidence on the existence of the Heaviside layer is still lacking."

* Smith-Rose and Barfield, 'Experimental Wireless,' September, 1925, p. 737.

The present paper deals with the same problem (*b*), but quite different experimental methods have been employed. Smith-Rose and Barfield sought to detect the down-coming waves by direction-finding methods, whereas we have studied the problem rather from the standpoint of intensity measurements, to which methods we were led by our study of radio signal fading.* The signal intensity measurement method possesses the advantage that the existence of the reflected wave at the ground at the receiving station does not prevent the detection of a down-coming wave, as it does in the directional method.

The evidence here presented for the direct experimental proof of the existence of the Heaviside layer is in two parts. In the first set of experiments it is shown that the signal variations usually known as "fading" are, in the cases of short-distance transmission, due to the interference of two or more rays arriving at the receiver with a definite path difference. But such experiments alone do not prove that any of the interfering rays are necessarily returned from the upper atmosphere, for it may be, and actually has been, objected that the path differences indicated by the experiments exist for rays travelling from the transmitter to the receiver in a horizontal plane, lateral deviation of one ray taking place due to the inhomogeneity of the earth's surface. A second set of experiments was therefore carried out, designed to test whether the interfering rays actually lie in a horizontal plane or not. It can be shown theoretically that, if the variable waves causing fading are returned from the upper atmosphere, the signal variations on a loop antenna should be relatively greater than those experienced on a vertical antenna at the same place. If the variable ray lies in a horizontal plane the reverse would be the case. The experimental test of this point is described in section 4 (*b*), and it is shown that the results can only be explained if we assume that the interfering rays come down from the upper atmosphere in the way suggested by the Heaviside layer theory.

2. Signal Variations in Short-Distance Transmissions.

The fact that temporal variations of signal intensity are experienced at night for short-wave transmissions is well known to many broadcast listeners. In a normal case of signal fluctuation, such as is experienced with a receiver 150 to 200 miles from a broadcasting station, the variation of signal intensity is so marked as to be noticeable in telephones. The Bureau of Standards in America

* *Vide* Appleton, 'Proc. Phys. Soc.,' vol. 37, Part 2, February, 1925; Appleton and Barnett, 'Nature,' March 7th, 1925; 'Electrician,' April 3rd, 1925, p. 398; 'Proc. Camb. Phil. Soc.,' vol. 22, Part 5, p. 674, 1925.

recently made an extensive study of such audible fading, and in the summary* of their results it is stated that very little definite evidence emerged from the analysis of the data collected by the various observers. One result of interest is, however, mentioned. It is stated that, when intensity and directional measurements were made simultaneously, no directional errors were found to accompany the signal fading. This has been interpreted by some investigators as indicating that directional errors and intensity variations are not both due to the action of rays returned from the upper atmosphere; and they have considered this conclusion as confirmed by the fact that there is no apparent correlation between directional errors and intensity variations when both phenomena are present and are observed simultaneously. A more detailed consideration of the problem shows, however, that if the ray returned from the upper atmosphere is, in general, elliptically polarized, as is suggested by the magneto-ionic theory proposed by the writers,† directional and signal variations may both occur, but have no apparent correlation, since they are separately due to the two rectangular components of the elliptically polarized ray, the phases and amplitudes of which need not necessarily be simply correlated.

It is clear at the outset that estimates of telephone signal audibility are unsatisfactory, and in the present experiments all measurements of signal variation have been galvanometric. The galvanometric method is at once more accurate and much more sensitive to variations than the audibility method, signal variations being registered which are quite undetectable in telephones. In this way fading has been studied at comparatively short distances (50 miles and less‡ from the transmitter), where a discussion of the possible causes of the effects is rendered simplest.

3. Preliminary Measurements.

The preliminary experiments, carried out at the Cavendish Laboratory, Cambridge, were made with an aerial of normal type which was directly coupled to a tuned high-frequency amplifier. Electro-magnetically coupled to the output circuit of the amplifier was a detector circuit with crystal rectifier and galvanometer. As care was taken for the amplifying triodes to function under conditions for which the characteristics were linear, we may assume that the oscillatory electromotive force impressed on the detector circuit was proportional to the amplitude of the received wave. If we further assume that the rectified

* 'Scientific Papers of the Bureau of Standards,' No. 476, vol. 19.

† Appleton and Barnett, *loc. cit.*

Pickard, 'Proc. Inst. Rad. Eng.,' vol. 12, No. 2, p. 119 (April, 1924).

current through the detector is proportional to the square of the voltage, the galvanometer reading may be considered proportional to the square of the intensity of the electric vector of the received carrier wave. A schematic diagram of the circuit used is shown in fig. 1, where the usual wireless diagrammatic conventions are employed.

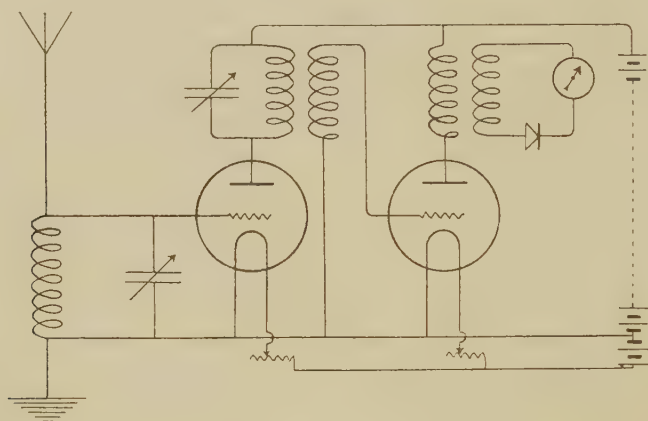


FIG. 1.

In measurements made on the signals from telephony stations accurate tuning is found to reduce the effect of modulation to a negligible amount.* To test this point in certain check experiments, fading was compared in periods when the transmitted wave was alternately modulated and unmodulated, and no difference was found. We found no support for Breit's conclusion† that fading is due to modulation.

In all the records obtained at Cambridge of the strength of the signals from London (2LO) it was found that the intensity remained fairly constant during the day, until about sunset, when small variations began and persisted through the night. A typical record for the sunset period‡ is shown in fig. 2, where the galvanometer readings are exhibited as a function of the time. Readings were taken every six seconds.

It will be noticed that, although variations occur, the mean galvanometer current is sensibly constant (except for the larger variations for which the

* This statement refers only to the short-wave stations of the British Broadcasting Company.

† Breit, 'Phys. Rev.,' vol. 25, No. 4, p. 589, April, 1925.

‡ Signal variations of exactly the same character were found to occur on the occasion of the solar eclipse on January 24th, 1925 ('Proc. Camb. Phil. Soc.,' *loc. cit.*).

mean current is slightly increased), which immediately suggests that the signal variations are brought about by interference between two rays, one of which is of changing phase and amplitude.

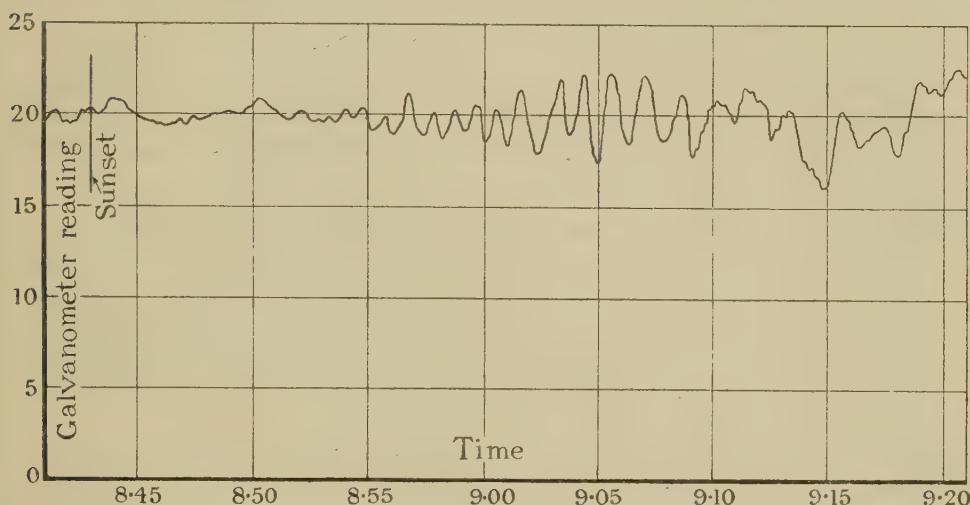


FIG. 2.

The following general theory has been proposed and found useful, both in our attempts to explain these results, and in suggesting experiments, described below, which were designed to test it. We have assumed that, for short-distance transmissions of the wave-lengths we are considering (*viz.*, 300–500 metres), rays of appreciable intensity may be returned at night from the upper atmosphere, which interfere with the direct or ground wave travelling from transmitter to receiver. Such atmospheric rays may have suffered one or more reflections, but for simplicity in explanation we shall, in what follows, consider the effect of the ray which has suffered only one reflection by the Heaviside layer. Such a theory postulates deviation of the indirect rays through large angles* (*e.g.*, through 120°), if the deviating stratum is

* The problem is thus quite different from the problem of long-distance transmission of long waves, where it is only necessary to assume that reflection takes place at very small glancing angles. Here the evidence for a conducting atmospheric layer is of quite a different character from that offered above. Van der Pol ('*Phil. Mag.*,' vol. 38, p. 365, September, 1919) showed that for long-distance transmission the signal intensities measured by Austin were many thousand times the value to be expected due to diffractive bending alone. Also the Marconi Company's Expedition results ('*Journ. Inst. Elect. Eng.*,' vol. 63, No. 346, p. 933, October, 1925) are found to agree very closely with Watson's transmission formula based on the reflection hypothesis.

supposed to be higher than say 50 kilometres. During the day-time the rays returned from the upper atmosphere are weak, due to their deviation in the lower layers of the atmosphere, where absorption is considerable, and the signal intensity is to be attributed mainly to the direct or ground ray. As the sun is setting the recombination of atmospheric ions takes place in the lower layers, where the pressure is high. The atmospheric rays are therefore deviated at higher levels of lower pressure, where collisional "friction" and its attendant absorption is small. In this way the stronger values of the reflected ray at night are accounted for. At night the ratio of the intensities of the reflected and ground rays increases with increase of distance. Thus at 50 miles the signal intensity is mainly due to the direct ray, both by day and by night. At about 100 miles the effects of the two rays are approximately equal, so that night-time interference phenomena are specially marked. At greater distances the signal is almost wholly due to the reflected ray and thus is much stronger at night than during the day.

The explanation of the effect of the interfering ray may be developed quantitatively as follows. Let us assume that the ground ray produces at the receiving station a vertical electric force $E_0 \sin pt$, so that the signal electromotive force v , impressed on the detector, is $\kappa E_0 \sin pt$, where κ is a constant. If the detector characteristic is represented by the equation

$$i = \alpha v + \beta v^2, \quad (1)$$

where i and v are the detector current and electromotive force, and α and β are constants, the mean signal current $\bar{i}$, which is measured by the galvanometer, is equal to $\frac{\beta \kappa^2 E_0^2}{2}$. At night, when the interfering ray is also present, we may assume that it produces another vertical electric force of magnitude $e \sin (pt + \theta)$ at the receiver, so that the total electromotive force acting on the detector will now be

$$\kappa \{E_0 \sin pt + e \sin (pt + \theta)\}.$$

In such a case the mean signal current $\bar{i}$, which is read on the galvanometer, will be the mean of

$$\beta \kappa^2 \{E_0 \sin pt + e \sin (pt + \theta)\}^2,$$

which is

$$\frac{\beta \kappa^2}{2} (E_0^2 + e^2 + 2E_0 e \cos \theta).$$

If, as is the case in the example we are considering, the vertical electric force due to the reflected ray is small compared with that due to the direct ray,

we may neglect e^2 in comparison with E_0^2 , and thus the *departure* of the signal current at night from its day-time value is $\beta\kappa^2 E_0 e \cos \theta$. The phase angle θ appears to vary within wide limits, so that its average value is zero, and thus the equality of the day and night mean values of signal current is explained.*

Since the direct ray is appreciably constant during the day there seems no reason why it should vary during the night, and thus the signal variations illustrated in fig. 2 above are to be attributed to the varying amplitude, polarization and phase† (relative to the direct ray) of the reflected ray or rays acting on a polarized receiver.

For transmission over greater distances the diurnal variation of signal current is somewhat different. Here the day-time strength is very weak, but at night the mean value is very much increased, remaining so throughout the night. The signal variations are not found to be as rapid as those experienced at shorter distances. In accordance with the general explanation given above we attribute the large increase of intensity at night to the large relative intensity of the rays deviated by the upper atmosphere, the direct ray being highly attenuated.‡ Fading in such cases may be almost complete, and is to be regarded as due to the varying amplitude, polarization and phase difference of the deviated rays acting on a polarized receiver.

4. *Experimental Proof of Existence of Atmospheric Deflecting Layer.*

(a) *Demonstration of Interference Phenomena indicating two or more Rays.*—

To test whether interference between the ground and atmospheric rays was really taking place in the manner suggested, the effect of changing the transmitter wave-length *continuously* through a small range was studied. It has already been mentioned that we had been led to the view that at a distance of about 100 miles from a transmitter the effect of the indirect ray approached in magnitude that of the direct ray, in which case interference phenomena would be very pronounced. Such a distance therefore seemed specially suitable for this experiment. As there was no suitable transmitter

* In cases where e^2 is not quite negligible compared with E_0^2 the increase of mean signal current is seen to be $\frac{\beta\kappa^2 e^2}{2}$.

† The increase in height of the under boundary of the layer about and after sunset will produce an alteration in the path difference of the rays and thus cause progressive interference phenomena at the earth's surface.

‡ The attenuation is due to the ground absorption and to the effect of the slight curvature of the earth, which for short wave-lengths is sufficient to prevent rectilinear propagation.

at this distance from Cambridge, the receiving station was moved to Oxford where excellent facilities were provided in the Electrical Laboratory by Prof. J. S. Townsend and Mr. E. W. B. Gill. The British Broadcasting Company very kindly loaned the use of the Bournemouth transmitter for two nights, after the normal broadcast programmes were finished. Capt. A. G. D. West, of the B.B.C., arranged the transmitter so that a known small change of wave-length $\delta\lambda$ (*e.g.*, 5 to 10 metres) could be uniformly produced in a given time (*e.g.*, 10 to 30 seconds), the aerial current remaining sensibly constant. No modulation of the wave took place during the experiment, land-line communication being used for control purposes. The receiver used at Oxford was a four-stage high-frequency amplifier, using tuned-anode coupling with specially wound coils of high resistance wire to produce very flat tuning. The signal currents were measured both by moving coil and small Einthoven galvanometers.

Two sets of experiments were carried out, on December 11, 1924, and on February 17, 1925, and on both occasions successions of interference maxima and minima were obtained as the wave-length was changed. These artificially produced maxima and minima were accompanied by the ordinary naturally-occurring variations, which occurred at a practically uniform rate throughout the period of the experiment and which, therefore, could be allowed for.

If we assume the simplest interpretation of these interference phenomena and regard them as analogous to those experienced in a Lloyd's mirror fringe system, the effects may be viewed somewhat as follows. If the ground ray path is a and the atmospheric ray path a' , the atmospheric ray arrives N wave-lengths behind as compared with the ground ray, where $N = \frac{a' - a}{\lambda}$, λ being the wave-length. If N is an integer the waves steadily reinforce, while if N is half-way between two integers they are steadily opposite in phase. If the wave-length is gradually increased to λ' at the transmitting station, the number of signal maxima n to be expected is

$$(a' - a) \left(\frac{1}{\lambda} - \frac{1}{\lambda'} \right), \quad \text{or} \quad \frac{\delta\lambda}{\lambda^2} (a' - a),$$

if the change of wave-length is very small. Since $\delta\lambda$ and λ are known, the value of $(a' - a)$ may be estimated.

It is not proposed here to give the results obtained in great detail, as experiments are to be made in which the signal current variations consequent on the wave-length change are to be photographically recorded. It is hoped,

in this way, to be able to make the wave-length change in about one second, during which time the natural variation of signal intensity should be negligible. Some results which are typical of the whole series may, however, be quoted. When the wave-length of the transmitter was changed through the range 385–392 metres the average number of fringes produced was 4·5. When the wave-length was from 385–395 metres the average number of fringes produced was 7·0. On substitution in the expression for N given above, both of these results indicate a value of $(a' - a)$ of the order of 100 kilometres, which would indicate that the layer is situated at a height of 80–90 kilometres. Besides the more prominent maxima and minima of intensity, which alone were counted (and which alone were seen on the somewhat sluggish moving coil galvanometer), subsidiary maxima and minima were noted on the string galvanometer. It seems quite possible that these were due to the effect of a ray which had suffered two deviations by the ionized layer together with reflection from the ground. The paths of such rays are illustrated in fig. 3, which is approximately to scale.

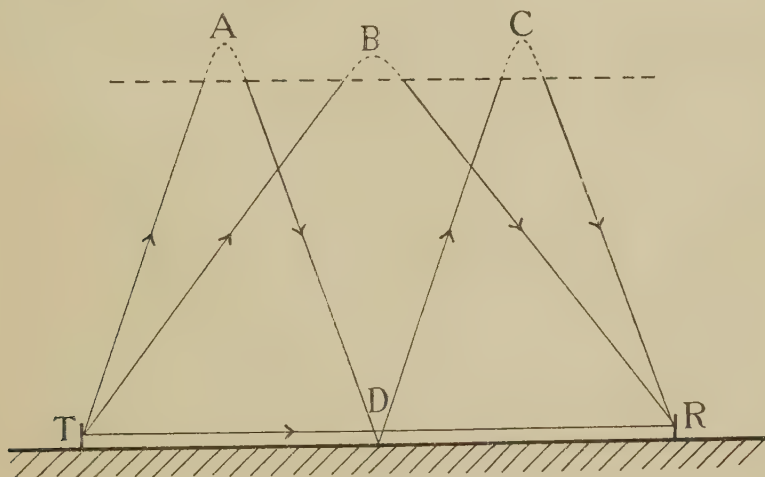


FIG. 3.

(b) *Measurement of the Angle at which Waves deviated by the Atmosphere reach the Ground.*—In considering the possible existence of rays reflected by the upper atmosphere and arriving at the ground in a direction inclined to the horizontal, it has been suggested* that maximum signal intensity would be obtained by tilting a vertical antenna until its direction is at right angles to

* Eccles, 'Roy. Soc. Proc.,' A, vol. 87 (1912).

the direction of propagation of the down-coming waves, in which case the angle of arrival could be estimated. It has similarly been suggested* that the signal received by a loop aerial will be zero when the axis of the loop coincides with the same direction of propagation. In such cases it appears to have been overlooked that a receiving station on the earth's surface is at the boundary between an insulator and a conductor, and, for the longer wavelengths, the interface acts almost as a perfect reflector. If waves from the atmosphere reach this boundary and are reflected, a stationary wave system is produced, and, in ordinary wireless measurements, we are concerned with the values of the electric and magnetic intensities within a region situated at the boundary, and of linear dimensions small compared with the wavelength of the radiation. It is easy to show† that in the case of a perfect conductor (and we assume this as a first approximation‡ in our case), an incident wave of arbitrary polarization from the atmosphere and a direct ground wave combine to produce vertical electric and horizontal magnetic forces. The horizontal electric force and the vertical magnetic force are zero. Thus the maximum signal with a straight wire aerial will always be obtained when the aerial is vertical, whatever may be the angle at which the waves reach the ground. Similarly the minimum signal with a loop aerial will always be obtained when its plane is horizontal.

In illustration of the present problem let us consider the effect of a ground wave together with a wave of arbitrary polarization arriving from the atmosphere at a point on the earth's surface. Let the plane in which propagation and atmospheric deviation§ take place be represented by the plane of the paper, and let the atmospheric wave reach the ground at an angle ϕ_1 as illustrated in fig. 4.

We consider the ground wave as having a vertical electric force of maximum amplitude E_0 . The atmospheric wave has maximum electric intensity E_1 in the plane of propagation, and E_1' at right angles. In all cases the electric vector is accompanied by a magnetic vector at right angles (H_0 , H_1 and H_1'

* Austin, 'Proc. Inst. Rad. Eng.,' vol. 13, No. 4, p. 410, August, 1925.

† Pierce, 'Electrical Oscillations and Electric Waves,' p. 397.

‡ Smith-Rose and Bartfield, *loc. cit.* The conductance of the surface layer (10^8 c.s.u.) is sufficient to turn back the waves with only very superficial penetration and with reflection not far from total. For very much shorter wave-lengths (*e.g.*, 10 metres) the reflection is by no means as marked.

§ For simplicity, this plane is assumed throughout to be vertical, but it seems quite possible that cases may occur in which this is not so, both lateral and vertical deviation of the atmospheric ray taking place.

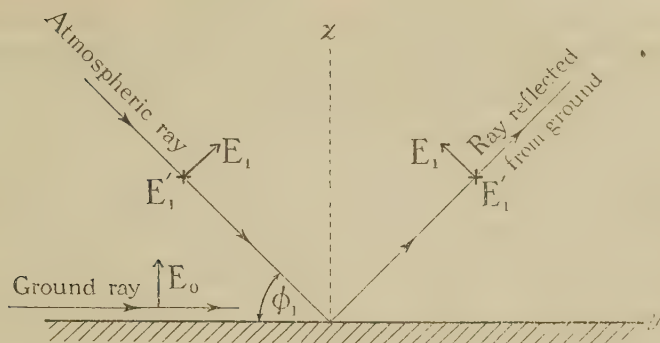


FIG. 4. The z axis is at right angles to the paper.

respectively), and, if the electric intensity is measured in electrostatic units and the magnetic intensity in electromagnetic units, we have numerically

$$E \equiv H. \quad (1)$$

We are concerned with the values of electric and magnetic intensity at the origin O . This is a simple problem of electromagnetic theory and the result only will be stated. This is most conveniently done by drawing the vectors in the plane of propagation (yz plane) and in the horizontal plane (xy plane). These are shown in fig. 5 and may be regarded as the elevation and plan of the system at O .

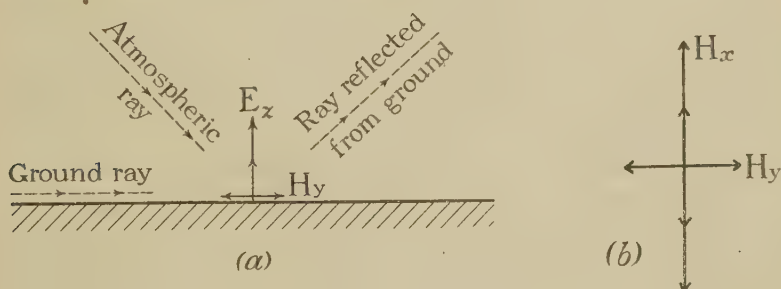


FIG. 5(a). $E_x = E_0 \sin pt + 2E_1 \cos \phi \cdot \sin (pt + \theta)$.

FIG. 5(b). $H_y = 2H_1' \sin \phi \cdot \sin (pt + \theta')$. $H_x = H_0 \sin pt + 2H_1 \sin (pt + \theta)$.

Let us suppose that we can compare the signals produced in a vertical wire aerial and in a loop in the plane of propagation (*i.e.*, with axis coincident with the axis of x). The signal in the vertical wire will be proportional to E_x and that in the loop to H_x . Thus in the day-time the aerial responds to a vertical electric force $E_0 \sin pt$, but at night this is increased to

$$E_0 \sin pt + 2E_1 \cos \phi \cdot \sin (pt + \theta)$$

(see fig. 5 (*a*)). The night-time departure* of signal current from the mean value is therefore $2\beta\kappa^2E_0E_1 \cos \phi \cdot \cos \theta$. On the other hand the magnetic force linked with the loop in the day-time is $H_0 \sin pt$ and at night

$$H_0 \sin pt + 2H_1 \sin (pt + \theta)$$

(see fig. 5 (*b*)). The night-time departure of signal current from the mean is therefore $2\beta_1\kappa_1^2H_0H_1 \cos \theta$, where β_1 and κ_1 , as before,† are constants depending on the detector and amplifier characteristics of the loop set. If now the two sets have been adjusted in the day-time so as to have the same amplification and sensitivity, we have

$$\frac{\beta\kappa^2E_0^2}{2} = \frac{\beta_1\kappa_1^2H_0^2}{2}. \quad (2)$$

Also, as in (1), we have

$$E_0 = H_0.$$

Thus R , the ratio of the departure of the night-time signal current from the day-time value on the loop set to the similar departure on the aerial set, is given by

$$R = \frac{\beta_1\kappa_1^2H_0H_1 \cos \theta}{\beta\kappa^2E_0E_1 \cos \phi_1 \cdot \cos \theta} = \sec \phi_1. \quad (3)$$

In other words, the signal variations on the loop set should be greater than on a vertical aerial receiver if the ray comes down from the upper atmosphere as postulated. On the other hand, if the interfering ray is laterally deviated in a horizontal plane and not vertically, it is easy to see that for the experimental conditions contemplated the reverse would be the case.

Experiments were therefore carried out to test this point. Signals were compared on a T-shaped aerial and on a large single-turn loop situated in the plane of propagation. The horizontal portion of the T-aerial was at right angles to the direction of propagation, so that the system had no resultant response to a horizontal electric vector at right angles to the plane of propagation. The plane of the T-aerial bisected the plane of the loop at right angles, thus ensuring minimum interaction. Two similar receiving sets were used, and the high-frequency amplifiers adjusted until the same galvanometer readings were obtained in the day-time. The ratio of the signal current variations from the mean day-time values were then observed when fading began. The preliminary experiments showed immediately that fading on the loop set was

* This is assumed to be small.

† See p. 626.

more pronounced than on the aerial set, indicating that the variations were due to rays arriving at the receiver in a direction inclined to the horizontal.

The first tests were made on the signals from London (2LO) at Cambridge, and it was observed that only when the two receiving aerials were very close together (centres not more than 90 feet apart) were the signal variations similar in phase in the two cases. Under these conditions it was possible to compare the deviations from the mean signal current for the same signal maxima and minima. The ratios of the loop signal variation to the corresponding aerial signal variation, for a large number of such maxima and minima, are exhibited in fig. 6, where the number of times (M) a particular ratio (R) was observed is plotted as a function of that ratio.

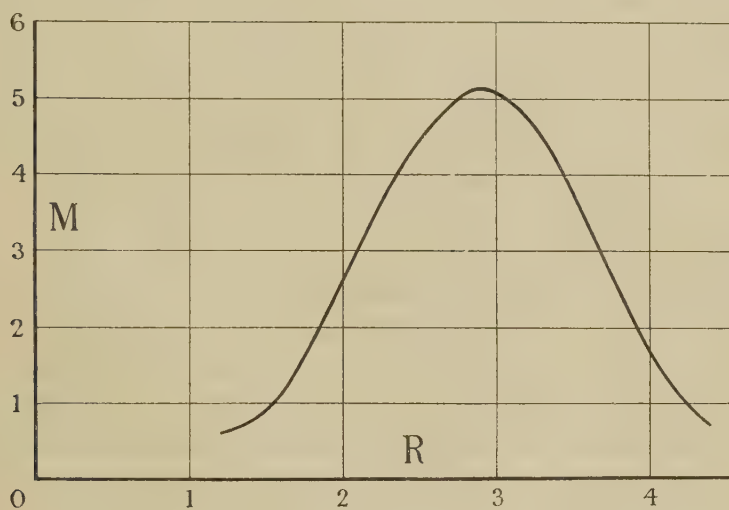


FIG. 6.

The maximum of the curve thus indicates the most frequent ratio observed. For these signals the ratio R was always found to be greater than unity, as is to be expected according to the deviating layer theory. The most frequent ratio is seen to be 2.85, which, with the simplifying assumption that there is only one atmospheric ray, indicates that the slope ϕ_1 is about 69° .

Further experiments were made with the two receiving sets much further apart, *e.g.*, 300 feet, and here it was found that the maxima and minima of signal intensity on the two sets did not appear to be simply correlated. It was, however, possible to take average departures of signal maxima and minima from the mean values during definite periods of observation, and again evidence of down-coming waves was obtained, the loop average being

consistently greater than the vertical aerial average, the ratios being similar to those obtained when the two receiving stations were closer together. The average value of the ratio for 156 sets of readings was found to be 2.2. This indicates a value of ϕ_1 equal to 63° .

Further experiments were made at Cambridge on the signals received from a more distant station at Birmingham (5IT), the transmitter being at a distance of 140 kilometres. Similar loop and aerial measurements were made, and it was found that again the average ratios were greater than unity. It was also found that the greater distance of transmission was not accompanied by any marked increase of signal variation, the percentage change of signal intensity being much less than that observed in the experiments at Oxford on the Bournemouth signals. This may be due to the difference in the "reflection" coefficient for the two wave-lengths (475 and 385 metres respectively) and to the difference in the attenuation of the two ground waves.

The average value of R for the Birmingham signals was 1.5, which indicates a value of 48° for ϕ_1 . The angle was therefore definitely smaller than that for the London signals, which is to be expected on account of the greater distance of transmission.

It was thought to be of interest to examine how the ratio of loop to aerial signal variation altered when the distance of transmission was very much reduced. This ratio should obviously increase rapidly as the distance of transmission is made smaller. Accordingly, galvanometric measurements were made at Potters Bar on the London signals, the distance of transmission being 12 miles. It was found that no signal variation could be detected on a vertical aerial, which was no doubt due to the fact that the effect of the ground ray was excessively large compared with the effect of the indirect ray. This interpretation indicated that the experiment ought to be repeated under conditions in which more rapid attenuation of the ground ray took place, and it was suggested by Mr. J. A. Ratcliffe that an excellent site for such an experiment would be at Rawtenstall, near Manchester, where he had found that the shielding effect of the intervening hills on the transmissions from Manchester (2ZY) produced excessive attenuation of the ground ray.

Experiments similar to those at Cambridge were therefore carried out at Rawtenstall on the Manchester transmissions, the distance being 18 miles. Here it was found that small signal fluctuations (of about 3 seconds period) took place during the day-time, the variations being of the order of 1 division in 20 on the galvanometer scale. For these variations it was found that the fluctuations were in phase and identical in magnitude on both loop and aerial

receivers. The cause of this variation, if not due to the transmitter, is obscure. At night the signal variations were much bigger on the loop system (*e.g.*, as much as 10 divisions in 20 on the galvanometer scale) and only slightly bigger on the aerial system, which again indicated the presence of down-coming rays. Owing to the effect of the variation which was observed in the day-time, and which presumably persisted at night, it is difficult to interpret the readings obtained quantitatively because of the superposition of the two effects. But in almost every case at night the ratio of the loop variation to the variation on the vertical aerial was greater than unity, ratios ranging between 7 and 1.5 being usual. Although no numerical deductions can be made from these figures, the fact that the loop variations were in general bigger than the aerial variations at night indicates that a down-coming ray has been observed at a distance as small as 18 miles from the transmitter. This is an example of reflection by the ionized layer at almost normal incidence.*

It has previously been shown by the writers that, according to the magneto-ionic theory of wave propagation, we may expect the rays returned from the upper atmosphere to be in general elliptically polarized, in which case both the horizontal vectors $2H_1$ and $2H_1' \sin \phi_1$ (see fig. 5 (b)) may be expected to be present in the stationary system at the surface of the ground. The results described above have only demonstrated the existence of the vector $2H_1$, since the plane of the loop in these experiments coincides with the plane of propagation. An experiment was therefore carried out at Cambridge on the London transmissions in which the signal variations were measured first with the loop in the plane of propagation and later with the plane of the loop still vertical, but inclined to the direction of propagation. A typical example of these results may be quoted. In one case with the loop pointing to the transmitter signal variations of 4 divisions in 30 were observed. When the loop was gradually turned through an angle of 45 degrees these signal variations increased to changes of 10 divisions in 30 on the galvanometer scale. Now a consideration of fig. 5 (b) shows that if $2H_1' \sin \phi_1$ is zero the relative effects of the magnetic vectors of the returned and ground rays ($2H_1$ and H_0 respectively) would be constant as the loop was rotated. The increase of signal variation proves that the horizontal vector $2H_1' \sin \phi_1$ in the plane of propagation was also present. We therefore conclude that the rays deviated by the upper atmosphere through

* It is of interest to note that reflection at normal incidence may be expected from an aerial with a horizontal portion. The radiation will penetrate the ionized layer to a point where the ionization is just sufficiently dense to make the refractive index (as calculated in terms of the magneto-ionic theory) complex, when total reflection takes place.

large angles have, in general, transverse components of magnetic intensity both in and at right angles to the plane of propagation, as is to be expected according to the magneto-ionic theory, in which the phase-velocity of the electromagnetic radiation is influenced by the earth's magnetic field. It is clear that the presence of the vector H_1' would give rise to errors in a direction-finder, as first suggested by Bellini* and Eckersley,† so that we may conclude that the directional errors experienced at night at distances as short as 30 miles are due to the upper atmosphere.

5. Discussion of Results.

The experiments described above have shown that the fluctuations of wireless signals observed in comparatively short-distance transmission are due to the variable nature of the rays which are deviated downwards through large angles by the upper atmosphere. The effects of these ionically reflected rays can be detected at distances as small as 18 miles from the transmitter. The significance of these results, and some deductions from them, are discussed below under sub-headings (a) to (d).

(a) *Diurnal Variation of Signal Intensity.*—It has been found that the signal variations usually become specially marked after sunset, but the correlation with the geometrical sunset is by no means marked throughout the whole year. For example, it is by no means marked in the winter, when small variations of increasing magnitude are observed some hours before sunset. In summer the introduction of the night-time variation is less gradual. This seasonal variation is in agreement with our general interpretation of the action of the layer, which is that the differences in its action are due mainly to the differences in height (and therefore pressure) of the effective stratum. The height in the day-time is assumed to be comparatively low (*e.g.*, 50 kilometres*), the ionization being maintained by solar action. This layer is at its lowest height at mid-day and in summer, when its action on wireless is least variable. At other times, *e.g.*, approaching sunset and also in winter, the sun's rays meet the earth's surface more obliquely and the layer is at a higher level, which we associate with the deviation of short waves with less absorption but with great variability. At

* Bellini, 'Electrician,' vol. 86, p. 220, February 18th, 1921.

† Eckersley, 'Radio Review,' vol. 2, pp. 60, and 231 (1921).

‡ For long-distance transmission on long waves the Marconi Company's Expedition results indicate that a day-time height of 40 kilometres must be assumed to make the data fit Watson's transmission formula ('Journ. Inst. Elect. Eng.,' *loc. cit.*). But for much shorter waves and very much shorter distances of transmission the effective stratum will be higher than this.

night, when the sun's influence is entirely removed, recombination of ions in the atmosphere proceeds further, and the height of the layer is increased, resulting in still less absorption and a higher coefficient of "reflection."

The determination of the height of the layer at night is somewhat indefinite because of the variability of the action of the layer. Moreover, an accurate estimate seems hardly possible in view of our inadequate knowledge of the trajectory of the rays at their highest points. But the general impression drawn from the data is that the night-time height is about 80–90 kilometres.

(b) *The Reflection Coefficient of the Ionized Layer.*—Since the experiments described above have given the relative order of magnitude of the direct and indirect waves, and also the angle at which the waves meet the layer, we can use the data to make an approximate estimate of the ratio ρ of the intensity of the emergent and incident rays at the surface of the deviating layer. The simplest conditions will be assumed.

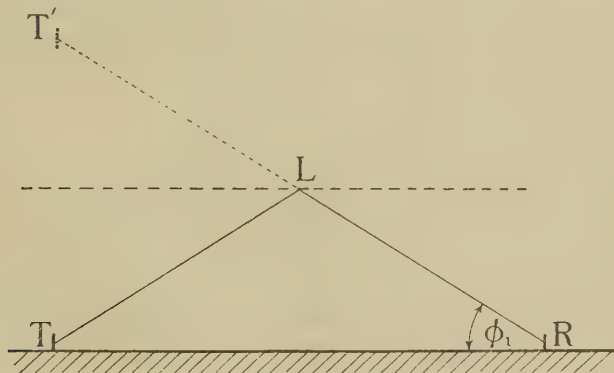


FIG. 7.

Let us assume that in fig. 7 T is a transmitter of effective height h and aerial current I , and thus of effective metre-amperes hI . We may consider the reflected ray reaching the receiver as that due to an imaginary transmitter of effective metre-amperes ρhI situated at T' , the position of the image of the transmitter in the ionized layer. We have to consider the relative amplitudes of the vertical electric forces due to the direct and indirect rays at the receiver R , which is situated at a distance $2D$ from the transmitter. The electric force due to the direct ray will be, in the absence of attenuation due to the ground, $\kappa hI/2D$, where κ is a constant. For the short wave-lengths we are considering, however, the ground absorption is considerable and must be taken into account. Data for this correction are available from the work of Bown and Gillett,* who have

* 'Proc. Inst. Rad. Eng.,' January 16th, 1924.

shown that the attenuation factor α in the Austin-Cohen coefficient of absorption varies between 0.01 and 0.035. If the Austin-Cohen coefficient is therefore used we find that the value of E_0 is given by

$$E_0 = \frac{\kappa I h}{2D} e^{-\alpha 2D/\sqrt{\lambda}},$$

where λ is the wave-length and λ and $2D$ are measured in kilometres. Now the intensity of the indirect ray at R, allowing for the obliquity of transmission, will be

$$\rho \frac{\kappa I h \cos^2 \phi_1}{2D},$$

and, assuming perfect reflection at the ground, the vertical electric force in the stationary wave system produced will be

$$2 \cos \phi_1 \left(\rho \frac{\kappa I h \cos^2 \phi_1}{2D} \right).$$

Thus the relative value of the vertical electric forces produced by the indirect and direct rays respectively (which determines the percentage of signal variation on a vertical antenna) is given by

$$2\rho \cos^3 \phi_1 e^{2\alpha D/\sqrt{\lambda}}.$$

Now the value of this ratio for the Cambridge measurements on the 2LO signals ($2D$ being 88 kilometres) is on the average 0.05, though it has been observed as high as 0.30, and ϕ_1 may be taken as about 65° , so that ρ , the coefficient of reflection of the layer, can be calculated. As previously mentioned, Bown and Gillett have found that α varies between 0.01 and 0.035 for different ground conditions. Accordingly the values of ρ for these extreme cases have been calculated. Using the former value of α , the atmospheric reflection coefficient is 6 per cent.; using the latter value it is 0.2 per cent.

(c) *Bearing of the Results on the Theory of Directional Errors.*—The experimental results at Cambridge indicated that the deviated ray was, in general, elliptically polarized, so that we must consider both magnetic vectors H_1 and H_1' to be present. If we assume, as seems reasonable, that the two vectors are of the same order of magnitude, it is possible to estimate approximately the error which would be produced in a loop direction finder of the ordinary type.

The magnitude of the error is easily shown to be $\tan^{-1} \frac{2H_1' \sin \phi_1}{H_0}$, for a case

where the direct wave is strong compared with the indirect wave. Now it has been shown above that at Cambridge for the 2LO signals

$$\frac{2H_1}{H_0} = 0.14,$$

and thus since we assume $H_1 \doteq H_1'$, the error δ is given by

$$\tan \delta = \frac{2H_1' \sin \phi_1}{H_0} = \frac{2H_1}{H_0} \sin \phi_1 = 0.14 \sin 65^\circ = \tan 7^\circ. \quad (4)$$

This indicates that quite appreciable directional errors due to rays deviated by the atmosphere are to be expected at distances as short as 50 miles from a transmitter over land, and we are thus justified in assuming that the directional errors which have been observed at 30 miles are due to the same cause.

(d) *Inferior Limit to N, the Number of Electric Carriers per Cubic Centimetre in the Ionized Layer.*—Since it has been proved that rays are deviated through large angles by the upper atmosphere, we may use the experimental data to calculate an inferior limit for the number N of the effective electrical carriers per cubic centimetre as follows. Consider a wireless ray from a transmitter T (see fig. 8) meeting the edge of the ionized layer with an angle of incidence i .

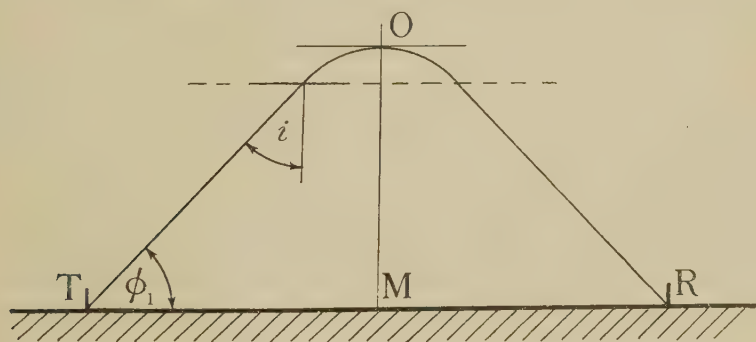


FIG. 8.

As the refractive index of the layer is supposed to decrease with height, the ray is deviated until it becomes horizontal at O . It is easily shown from the ordinary principles of optics that if μ is the refractive index at O , and μ_0 the refractive index of the air below the ionized stratum,

$$\mu_0 \sin i = \mu \sin \frac{\pi}{2} = \mu. \quad (5)$$

Now the value of μ has been shown* to be largely dependent on the earth's magnetic field, if the carriers are electrons, except in cases where the frequency of the radiation is large compared with a certain critical frequency. This critical frequency is the frequency with which the free electrons spiral round the lines of magnetic force, and is equal to $Te/2\pi m$, where T is the earth's total

* Appleton, *loc. cit.*

magnetic force. The critical frequency corresponds in England to a critical wave-length of about 220 metres. The path of the rays for wave-lengths round about this critical value, such as we have used in the experiments described above, is somewhat difficult to estimate, but for the 20-metre wave-length transmissions used by amateurs no such difficulty arises. For such short wave-lengths we may write

$$\mu^2 = 1 - \frac{4\pi N e^2}{m p^2} \quad (6)$$

where N is the number of electrons per cubic centimetre, e and m the charge and mass of the electron, and p the angular frequency of the radiation. Thus as μ_0 may be considered unity, we find that

$$\sin^2 \phi = \frac{4\pi N e^2}{m p^2} \quad (7)$$

Now it is known that 20-metre transmissions are not heard at all strongly at a distance of 100 miles, but that at about 400 miles the intensity increases again. In accordance with the view of short-distance transmission adopted throughout this paper, we interpret this as indicating that the direct ray is strongly attenuated along the ground, and it is only when the indirect rays are deviated without undue absorption that signals are again obtained. Thus in the example illustrated in fig. 8 we may take TR as 400 miles and OM as 30 miles approximately. Thus $\sin \phi$ is 0.15, and on substituting in (7) and taking p as 10^8 we find that the inferior limit of N is of the order of 10^5 electrons per cubic centimetre. The actual value is likely to be much greater than the inferior limit. In the derivation of the formula used above for the refractive index the effect of collisional "friction" has been neglected. It is easily shown, however, that if frictional absorption is appreciable the value of N must be greater than that found in the simple case given above.

6. *Summary of Results.*

(1) Experiments are described which indicate that, for short-distance transmission of short wireless waves, the "fading" of signals is due to interference of ground waves and waves deviated through large angles by the upper atmosphere. The phenomena are similar to those of a Lloyd's mirror fringe system. A method of estimating the path difference of the rays is described.

(2) It is shown that if the variable rays causing "fading" arrive at the receiver in a downward direction (*i.e.*, inclined to the horizontal) signal

variations should be more pronounced on a loop aerial than on a vertical antenna. Experimental tests show that this is the case, and that for the London to Cambridge transmissions the rays returned from the upper atmosphere arrive at an angle of 60° – 70° with the ground.

(3) An examination of the stationary wave system produced when the atmospheric rays reach and are reflected by the ground shows that the atmospheric rays are, in general, elliptically polarized. Such polarization is to be expected according to the magneto-ionic theory of atmospheric refraction. The elliptically polarized rays are shown to be of sufficient intensity to cause errors in direction-finders at very short distances (*e.g.*, 30–50 miles) for over-land transmission.

(4) The reflection coefficient of the ionized layer for low angles of incidence is shown to lie between the limits 0·2 per cent. and 6 per cent., according to the attenuation factor assumed for the ground ray.

(5) An inferior limit for the number of electrons per cubic centimetre in the ionized layer is shown to be 10^5 .

In conclusion, we should like to express our gratitude to Prof. Sir Ernest Rutherford for providing facilities for these experiments and for many helpful suggestions, and also to Prof. Sir Joseph Larmor for advice on many theoretical points in connection with the interpretation of results. We are very much indebted to Mr. J. A. Ratcliffe, of the Cavendish Laboratory, for assisting us in the greater part of the experimental work.

The Fundamental Equations of Quantum Mechanics.

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§ 1. *Introduction.*

It is well known that the experimental facts of atomic physics necessitate a departure from the classical theory of electrodynamics in the description of atomic phenomena. This departure takes the form, in Bohr's theory, of the special assumptions of the existence of stationary states of an atom, in which it does not radiate, and of certain rules, called quantum conditions, which fix the stationary states and the frequencies of the radiation emitted during transitions between them. These assumptions are quite foreign to the classical theory, but have been very successful in the interpretation of a restricted region of atomic phenomena. The only way in which the classical theory is used is through the assumption that the classical laws hold for the description of the motion in the stationary states, although they fail completely during transitions, and the assumption, called the Correspondence Principle, that the classical theory gives the right results in the limiting case when the action per cycle of the system is large compared to Planck's constant h , and in certain other special cases.

In a recent paper* Heisenberg puts forward a new theory, which suggests that it is not the equations of classical mechanics that are in any way at fault, but that the mathematical operations by which physical results are deduced from them require modification. All the information supplied by the classical theory can thus be made use of in the new theory.

§ 2. *Quantum Algebra.*

Consider a multiply periodic non-degenerate dynamical system of u degrees of freedom, defined by equations connecting the co-ordinates and their time differential coefficients. We may solve the problem on the classical theory in the following way. Assume that each of the co-ordinates x can be expanded in the form of a multiple Fourier series in the time t , thus,

$$\begin{aligned} x &= \sum_{\alpha_1 \dots \alpha_u} x_{\alpha} (\alpha_1 \alpha_2 \dots \alpha_u) \exp. i (\alpha_1 \omega_1 + \alpha_2 \omega_2 + \dots + \alpha_u \omega_u) t \\ &= \sum_{\alpha} x_{\alpha} \exp. i (\alpha \omega) t, \end{aligned}$$

* Heisenberg, 'Zeits. f. Phys.,' vol. 33, p. 879 (1925).

say, for brevity. Substitute these values in the equations of motion, and equate the coefficients on either side of each harmonic term. The equations obtained in this way (which we shall call the A equations) will determine each of the amplitudes x_a and frequencies $(\alpha\omega)$, (the frequencies being measured in radians per unit time). The solution will not be unique. There will be a u -fold infinity of solutions, which may be labelled by taking the amplitudes and frequencies to be functions of u constants $\kappa_1 \dots \kappa_u$. Each x_a and $(\alpha\omega)$ is now a function of two sets of numbers, the α 's and the κ 's, and may be written $x_{\alpha\kappa}, (\alpha\omega)_{\kappa}$.

In the quantum solution of the problem, according to Heisenberg, we still assume that each co-ordinate can be represented by harmonic components of the form $\exp. i\omega t$, the amplitude and frequency of each depending on two sets of numbers $n_1 \dots n_u$ and $m_1 \dots m_u$, in this case all integers, and being written $x(nm), \omega(nm)$. The differences $n_r - m_r$ correspond to the previous α_r , but neither the n 's nor any functions of the n 's and m 's play the part of the previous κ 's in pointing out to which solution each particular harmonic component belongs. We cannot, for instance, take together all the components for which the n 's have a given set of values, and say that these by themselves form a single complete solution of the equations of motion. The quantum solutions are all interlocked, and must be considered as a single whole. The effect of this mathematically is that, while on the classical theory each of the A equations is a relation between amplitudes and frequencies having one particular set of κ 's, the amplitudes and frequencies occurring in a quantum A equation do not have one particular set of values for the n 's, or for any functions of the n 's and m 's, but have their n 's and m 's related in a special way, which will appear later.

On the classical theory we have the obvious relation

$$(\alpha\omega)_{\kappa} + (\beta\omega)_{\kappa} = (\alpha + \beta, \omega)_{\kappa}.$$

Following Heisenberg, we assume that the corresponding relation on the quantum theory is

$$\omega(n, n - \alpha) + \omega(n - \alpha, n - \alpha - \beta) = \omega(n, n - \alpha - \beta)$$

or

$$\omega(nm) + \omega(mk) = \omega(nk). \quad (1)$$

This means that $\omega(nm)$ is of the form $\Omega(n) - \Omega(m)$, the Ω 's being frequency levels. On Bohr's theory these would be $2\pi/\hbar$ times the energy levels, but we do not need to assume this.

On the classical theory we can multiply two harmonic components related to the same set of κ 's, as follows :—

$$a_{\alpha\kappa} \exp. i (\alpha\omega)_{\kappa} t . b_{\beta\kappa} \exp. i (\beta\omega)_{\kappa} t = (ab)_{\alpha+\beta, \kappa} \exp. i (\alpha + \beta, \omega)_{\kappa} t$$

where

$$(ab)_{\alpha+\beta, \kappa} = a_{\alpha\kappa} b_{\beta\kappa}.$$

In a corresponding manner on the quantum theory we can multiply an (nm) and an (mk) component

$$a (nm) \exp. i \omega (nm) t . b (mk) \exp. i \omega (mk) t = ab (nk) \exp. i \omega (nk) t$$

where

$$ab (nk) = a (nm) b (mk).$$

We are thus led to consider the product of the amplitudes of an (nm) and an (mk) component as an (nk) amplitude. This, together with the rule that only amplitudes related to the same pair of sets of numbers can occur added together in an A equation, replaces the classical rule that all amplitudes occurring in an A equation have the same set of κ 's.

We are now in a position to perform the ordinary algebraic operations on quantum variables. The sum of x and y is determined by the equations

$$\{x + y\} (nm) = x (nm) + y (nm)$$

and the product by

$$xy (nm) = \sum_k x(nk) y (km) \quad (2)$$

similar to the classical product

$$(xy)_{\alpha\kappa} = \sum_r x_{r\kappa} y_{\alpha-r, \kappa}.$$

An important difference now occurs between the two algebras. In general

$$xy (nm) \neq yx (nm)$$

and quantum multiplication is not commutative, although, as is easily verified, it is associative and distributive. The quantity with components $xy (nm)$ defined by (2) we shall call the Heisenberg product of x and y , and shall write simply as xy . Whenever two quantum quantities occur multiplied together, the Heisenberg product will be understood. Ordinary multiplication is, of course, implied in the products of amplitudes and frequencies and other quantities that are related to sets of n 's which are explicitly stated.

The reciprocal of a quantum quantity x may be defined by either of the relations

$$1/x . x = 1 \quad \text{or} \quad x . 1/x = 1. \quad (3)$$

These two equations are equivalent, since if we multiply both sides of the

former by x in front and divide by x behind we get the latter. In a similar way the square root of x may be defined by

$$\sqrt{x} \cdot \sqrt{x} = x. \quad (4)$$

It is not obvious that there always should be solutions to (3) and (4). In particular, one may have to introduce sub-harmonics, *i.e.*, new intermediate frequency levels, in order to express $\sqrt{x}$. One may evade these difficulties by rationalising and multiplying up each equation before interpreting it on the quantum theory and obtaining the A equations from it.

We are now able to take over each of the equations of motion of the system into the quantum theory provided we can decide the correct order of the quantities in each of the products. Any equation deducible from the equations of motion by algebraic processes not involving the interchange of the factors of a product, and by differentiation and integration with respect to t , may also be taken over into the quantum theory. In particular, the energy equation may be thus taken over.

The equations of motion do not suffice to solve the quantum problem. On the classical theory the equations of motion do not determine the $x_{\alpha\kappa}$, $(\alpha\omega)_{\kappa}$ as functions of the κ 's until we assume something about the κ 's which serves to define them. We could, if we liked, complete the solution by choosing the κ 's such that $\partial E / \partial \kappa_r = \omega_r / 2\pi$, where E is the energy of the system, which would make the κ_r equal the action variables J_r . There must be corresponding equations on the quantum theory, and these constitute the quantum conditions.

§ 3. *Quantum Differentiation.*

Up to the present the only differentiation that we have considered on the quantum theory is that with respect to the time t . We shall now determine the form of the most general quantum operation d/dv that satisfies the laws

$$\frac{d}{dv} (x + y) = \frac{d}{dv} x + \frac{d}{dv} y, \quad (I)$$

and

$$\frac{d}{dv} (xy) = \frac{d}{dv} x \cdot y + x \cdot \frac{d}{dv} y. \quad (II)$$

(Note that the order of x and y is preserved in the last equation.)

The first of these laws requires that the amplitudes of the components of dx/dv shall be linear functions of those of x , *i.e.*,

$$dx/dv (nm) = \sum_{n'm'} a (nm; n'm') x (n'm'). \quad (5)$$

There is one coefficient $a(nm; n'm')$ for any four sets of integral values for the n 's, m 's, n 's and m 's. The second law imposes conditions on the a 's. Substitute for the differential coefficients in II their values according to (5) and equate the (nm) components on either side. The result is

$$\sum_{n'm'k} a(nm; n'm') x(n'k) y(km') = \sum_{kn'k'} a(nk; n'k') x(n'k') y(km) \\ + \sum_{kk'm} x(nk) a(km; k'm') y(k'm').$$

This must be true for all values of the amplitudes of x and y , so that we can equate the coefficients of $x(n'k) y(k'm')$ on either side. Using the symbol δ_{mn} to have the value unity when $m = n$ (i.e., when each $m_r = n_r$) and zero when $m \neq n$, we get

$$\delta_{kk'} a(nm; n'm') = \delta_{mm'} a(nk'; n'k) + \delta_{nn'} a(km; k'm').$$

To proceed further, we have to consider separately the various cases of equality and inequality between the kk' , mm' and nn' .

Take first the case when $k = k'$, $m \neq m'$, $n \neq n'$. This gives

$$a(nm; n'm') = 0.$$

Hence all the $a(nm; n'm')$ vanish except those for which either $n = n'$ or $m = m'$ (or both). The cases $k \neq k'$, $m = m'$, $n \neq n'$ and $k \neq k'$, $m \neq m'$, $n = n'$ do not give us anything new. Now take the case $k = k'$, $m = m'$, $n \neq n'$. This gives

$$a(nm; n'm) = a(nk; n'k).$$

Hence $a(nm; n'm)$ is independent of m provided $n \neq n'$. Similarly, the case $k = k'$, $m \neq m'$, $n = n'$ tells us that $a(nm; nm')$ is independent of n provided $m \neq m'$. The case $k \neq k'$, $m = m'$, $n = n'$ now gives

$$a(nk'; nk) + a(km; k'm) = 0.$$

We can sum up these results by putting

$$a(nk'; nk) = a(kk') = -a(km; k'm), \quad (6)$$

provided $k \neq k'$. The two-index symbol $a(kk')$ depends, of course, only on the two sets of integers k and k' . The only remaining case is $k = k'$, $m = m'$, $n = n'$, which gives

$$a(nm; nm) = a(nk; nk) + a(km; km).$$

This means we can put

$$a(nm; nm) = a(mm) - a(nn). \quad (7)$$

Equation (7) completes equation (6) by defining $a(kk')$ when $k = k'$.

Equation (5) now reduces to

$$\begin{aligned} dx/dv (nm) &= \sum_{m' \neq m} a (nm; nm') x (nm') + \sum_{n' \neq n} a (nm; n'm) x (n'm) \\ &\quad + a (nm; nm) x (nm) \\ &= \sum_{m' \neq m} a (m'm) x (nm') - \sum_{n' \neq n} a (nn') x (n'm) \\ &\quad + \{a (nm) - a (nn)\} x (nm) \\ &= \sum_k \{x (nk) a (km) - a (nk) x (km)\}. \end{aligned}$$

Hence

$$dx/dv = xa - ax. \quad (8)$$

Thus the most general operation satisfying the laws I and II that one can perform upon a quantum variable is that of taking the difference of its Heisenberg products with some other quantum variable. It is easily seen that one cannot in general change the order of differentiations, *i.e.*,

$$\frac{d^2x}{du dv} \neq \frac{d^2x}{dv du}.$$

As an example in quantum differentiation we may take the case when (a) is a constant, so that $a (nm) = 0$ except when $n = m$. We get

$$dx/dv (nm) = x (nm) a (mm) - a (nn) x (nm).$$

In particular, if $ia (mm) = \Omega (m)$, the frequency level previously introduced, we have

$$dx/dv (nm) = i\omega (nm) x (nm),$$

and our differentiation with respect to v becomes ordinary differentiation with respect to t .

§ 4. The Quantum Conditions.

We shall now consider to what the expression $(xy - yx)$ corresponds on the classical theory. To do this we suppose that $x (n, n - \alpha)$ varies only slowly with the n 's, the n 's being large numbers and the α 's small ones, so that we can put

$$x (n, n - \alpha) = x_{\alpha\kappa}$$

where $\kappa_r = n_r \hbar$ or $(n_r + \alpha_r) \hbar$, these being practically equivalent. We now have

$$\begin{aligned} &x (n, n - \alpha) y (n - \alpha, n - \alpha - \beta) - y (n, n - \beta) x (n - \beta, n - \alpha - \beta) \\ &= \{x (n, n - \alpha) - x (n - \beta, n - \beta - \alpha)\} y (n - \alpha, n - \alpha - \beta) \\ &\quad - \{y (n, n - \beta) - y (n - \alpha, n - \alpha - \beta)\} x (n - \beta, n - \alpha - \beta). \\ &= \hbar \sum_r \left\{ \beta_r \frac{\partial x_{\alpha\kappa}}{\partial \kappa_r} y_{\beta\kappa} - \alpha_r \frac{\partial y_{\beta\kappa}}{\partial \kappa_r} x_{\alpha\kappa} \right\}. \end{aligned} \quad (9)$$

Now

$$2\pi i \beta_r y_\beta \exp. i(\beta \omega) t = \frac{\partial}{\partial w_r} \{y_\beta \exp. i(\beta \omega) t\}$$

where the w_r are the angle variables, equal to $\omega_r t / 2\pi$. Hence the (nm) component of $(xy - yx)$ corresponds on the classical theory to

$$\begin{aligned} \frac{i\hbar}{2\pi} \Sigma_{\alpha+\beta=n-m} \Sigma_r \left\{ \frac{\partial}{\partial \kappa_r} \{x_\alpha \exp. i(\alpha \omega) t\} \frac{\partial}{\partial w_r} \{y_\beta \exp. i(\beta \omega) t\} \right. \\ \left. - \frac{\partial}{\partial \kappa_r} \{y_\beta \exp. i(\beta \omega) t\} \frac{\partial}{\partial w_r} \{x_\alpha \exp. i(\alpha \omega) t\} \right\} \end{aligned}$$

or $(xy - yx)$ itself corresponds to

$$-\frac{i\hbar}{2\pi} \Sigma_r \left\{ \frac{\partial x}{\partial \kappa_r} \frac{\partial y}{\partial w_r} - \frac{\partial y}{\partial \kappa_r} \frac{\partial x}{\partial w_r} \right\}.$$

If we make the κ_r equal the action variables J_r , this becomes $i\hbar/2\pi$ times the Poisson (or Jacobi) bracket expression

$$[x, y] = \Sigma_r \left\{ \frac{\partial x}{\partial w_r} \frac{\partial y}{\partial J_r} - \frac{\partial y}{\partial w_r} \frac{\partial x}{\partial J_r} \right\} = \Sigma_r \left\{ \frac{\partial x}{\partial q_r} \frac{\partial y}{\partial p_r} - \frac{\partial y}{\partial q_r} \frac{\partial x}{\partial p_r} \right\}$$

where the p 's and q 's are any set of canonical variables of the system.

The elementary Poisson bracket expressions for various combinations of the p 's and q 's are

$$\left. \begin{aligned} [q_r, q_s] &= 0, & [p_r, p_s] &= 0, \\ [q_r, p_s] &= \delta_{rs} = 0 & (r \neq s) \\ &= 1. & (r = s) \end{aligned} \right\} \quad (10)$$

The general bracket expressions satisfy the laws I and II, which now read

$$\begin{aligned} [x, z] + [y, z] &= [x + y, z], & \text{IA} \\ [xy, z] &= [x, z]y + x[y, z]. & \text{IIA} \end{aligned}$$

By means of these laws, together with $[x, y] = -[y, x]$, if x and y are given as algebraic functions of the p_r and q_r , $[x, y]$ can be expressed in terms of the $[q_r, q_s]$, $[p_r, p_s]$ and $[q_r, p_s]$, and thus evaluated, without using the commutative law of multiplication (except in so far as it is used implicitly on account of the proof of IIA requiring it). The bracket expression $[x, y]$ thus has a meaning on the quantum theory when x and y are quantum variables, if we take the elementary bracket expressions to be still given by (10).

We make the fundamental assumption that *the difference between the Heisenberg products of two quantum quantities is equal to $i\hbar/2\pi$ times their Poisson bracket expression*. In symbols,

$$xy - yx = i\hbar/2\pi \cdot [x, y]. \quad (11)$$

We have seen that this is equivalent, in the limiting case of the classical theory, to taking the arbitrary quantities κ_r that label a solution equal to the J_r , and it seems reasonable to take (11) as constituting the general quantum conditions.

It is not obvious that all the information supplied by equation (11) is consistent. Owing to the fact that the quantities on either side of (11) satisfy the same laws I and II or IA and IIA, the only independent conditions given by (11) are those for which x and y are p 's or q 's, namely

$$\left. \begin{aligned} q_r q_s - q_s q_r &= 0 \\ p_r p_s - p_s p_r &= 0 \\ q_r p_s - p_s q_r &= \delta_{rs} i\hbar/2\pi \end{aligned} \right\}. \quad (12)$$

If the only grounds for believing that the equations (12) were consistent with each other and with the equations of motion were that they are known to be consistent in the limit when $\hbar \rightarrow 0$, the case would not be very strong, since one might be able to deduce from them the inconsistency that $\hbar = 0$, which would not be an inconsistency in the limit. There is much stronger evidence than this, however, owing to the fact that the classical operations obey the same laws as the quantum ones, so that if, by applying the quantum operations, one can get an inconsistency, by applying the classical operations in the same way one must also get an inconsistency. If a series of classical operations leads to the equation $0 = 0$, the corresponding series of quantum operations must also lead to the equation $0 = 0$, and not to $\hbar = 0$, since there is no way of obtaining a quantity that does not vanish by a quantum operation with quantum variables such that the corresponding classical operation with the corresponding classical variables gives a quantity that does vanish. The possibility mentioned above of deducing by quantum operations the inconsistency $\hbar = 0$ thus cannot occur. *The correspondence between the quantum and classical theories lies not so much in the limiting agreement when $\hbar \rightarrow 0$ as in the fact that the mathematical operations on the two theories obey in many cases the same laws.*

For a system of one degree of freedom, if we take $p = m\dot{q}$, the only quantum condition is

$$2\pi m (q\dot{q} - \dot{q}q) = i\hbar.$$

Equating the constant part of the left-hand side to $i\hbar$, we get

$$4\pi m \sum_k q(nk) q(kn) \omega(kn) = \hbar.$$

This is equivalent to Heisenberg's quantum condition.* By equating the remaining components of the left-hand side to zero we get further relations not given by Heisenberg's theory.

The quantum conditions (12) get over, in many cases, the difficulties concerning the order in which quantities occurring in products in the equations of motion are to be taken. The order does not matter except when a p_r and q are multiplied together, and this never occurs in a system describable by a potential energy function that depends only on the q 's, and a kinetic energy function that depends only on the p 's.

It may be pointed out that the classical theory quantity occurring in Kramers' and Heisenberg's theory of scattering by atoms† has components which are of the form (8) (with $\kappa_r = J_r$), and which are interpreted on the quantum theory in a manner in agreement with the present theory. No classical expression involving differential coefficients can be interpreted on the quantum theory unless it can be put into this form.

§ 5. *Properties of the Quantum Poisson Bracket Expressions.*

In this section we shall deduce certain results that are independent of the assumption of the quantum conditions (11) or (12).

The Poisson bracket expressions satisfy on the classical theory the identity

$$[x, y, z] \equiv [[x, y], z] + [[y, z], x] + [[z, x], y] = 0. \quad (13)$$

On the quantum theory this result is obviously true when x , y and z are p 's or q 's. Also, from IA and IIA

$$[x_1 + x_2, y, z] = [x_1, y, z] + [x_2, y, z]$$

and

$$[x_1, x_2, y, z] = x_1 [x_2, y, z] + [x_1, y, z] x_2.$$

Hence the result must still be true on the quantum theory when x , y and z are expressible in any way as sums and products of p 's and q 's, so that it must be generally true. Note that the identity corresponding to (13) when the Poisson bracket expressions are replaced by the differences of the Heisenberg products ($xy - yx$) is obviously true, so that there is no inconsistency with equation (11).

If H is the Hamiltonian function of the system, the equations of motion may be written classically

$$\dot{p}_r = [p_r, H] \qquad \dot{q}_r = [q_r, H].$$

* Heisenberg, *loc. cit.* equation (16).

† Kramers and Heisenberg, 'Zeits. f. Phys.,' vol. 31, p. 681, equation (18), (1925).

These equations will be true on the quantum theory for systems for which the orders of the factors of products occurring in the equations of motion are unimportant. They may be taken to be true for systems for which these orders are important if one can decide upon the orders of the factors in H . From laws IA and IIA it follows that

$$\dot{x} = [x, H] \quad (14)$$

on the quantum theory for any x .

If A is an integral of the equations of motion on the quantum theory, then

$$[A, H] = 0.$$

The action variables J_r must, of course, satisfy this condition. If A_1 and A_2 are two such integrals, then, by a simple application of (13), it follows that

$$[A_1, A_2] = \text{const.}$$

as on the classical theory.

The conditions on the classical theory that a set of variables P_r, Q_r shall be canonical are

$$[Q_r, Q_s] = 0 \quad [P_r, P_s] = 0$$

$$[Q_r, P_s] = \delta_{rs}.$$

These equations may be taken over into the quantum theory as the conditions for the quantum variables P_r, Q_r to be canonical.

On the classical theory we can introduce the set of canonical variables ξ_r, η_r related to the uniformising variables J_r, w_r by

$$\xi_r = (2\pi)^{-\frac{1}{2}} J_r^{\frac{1}{2}} \exp. 2\pi i w_r, \quad \eta_r = -i (2\pi)^{-\frac{1}{2}} J_r^{\frac{1}{2}} \exp. - 2\pi i w_r.$$

Presumably there will be a corresponding set of canonical variables on the quantum theory, each containing only one kind of component, so that $\xi_r(nm) = 0$ except when $m_r = n_r - 1$ and $m_s = n_s$ ($s \neq r$), and $\eta_r(nm) = 0$ except when $m_r = n_r + 1$ and $m_s = n_s$ ($s \neq r$). One may consider the existence of such variables as the condition for the system to be multiply periodic on the quantum theory. The components of the Heisenberg products of ξ_r and η_r satisfy the relation

$$\xi_r \eta_r (nn) = \xi_r (nm) \eta_r (mn) = \eta_r (mn) \xi_r (nm) = \eta_r \xi_r (mm) \quad (15)$$

where the m 's are related to the n 's by the formulæ $m_r = n_r - 1$, $m_s = n_s$ ($s \neq r$).

The classical ξ 's and η 's satisfy $\xi_r \eta_r = -i/2\pi \cdot J_r$. This relation does not necessarily hold between the quantum ξ 's and η 's. The quantum relation

may, for instance, be $\eta_r \xi_r = -i/2\pi \cdot J_r$, or $\frac{1}{2}(\xi_r \eta_r + \eta_r \xi_r) = -i/2\pi \cdot J_r$. A detailed investigation of any particular dynamical system is necessary in order to decide what it is. In the event of the last relation being true, we can introduce the set of canonical variables ξ_r', η_r' defined by

$$\xi_r' = (\xi_r + i\eta_r)/\sqrt{2}, \quad \eta_r' = (i\xi_r + \eta_r)/\sqrt{2},$$

and shall then have

$$J_r = \pi (\xi_r'^2 + \eta_r'^2).$$

This is the case that actually occurs for the harmonic oscillator. In general J_r is not necessarily even a rational function of the ξ_r and η_r , an example of this being the rigid rotator considered by Heisenberg.

§ 6. *The Stationary States.*

A quantity C , that does not vary with the time, has all its (nm) components zero, except those for which $n = m$. It thus becomes convenient to suppose each set of n 's to be associated with a definite state of the atom, as on Bohr's theory, so that each $C(nn)$ belongs to a certain state in precisely the same way in which *every* quantity occurring in the classical theory belongs to a certain configuration. The components of a varying quantum quantity are so interlocked, however, that it is impossible to associate the sum of certain of them with a given state.

A relation between quantum quantities reduces, when all the quantities are constants, to a relation between $C(nn)$'s belonging to a definite stationary state n . This relation will be the same as the classical theory relation, on the assumption that the classical laws hold for the description of the stationary states; in particular, the energy will be the same function of the J 's as on the classical theory. We have here a justification for Bohr's assumption of the mechanical nature of the stationary states. It should be noted though, that the variable quantities associated with a stationary state on Bohr's theory, the amplitudes and frequencies of orbital motion, have no physical meaning and are of no mathematical importance.

If we apply the fundamental equation (11) to the quantities x and H we get, with the help of (14),

$$x(nm)H(mm) - H(nn)x(nm) = i\hbar/2\pi \cdot \dot{x}(nm) = -\hbar/2\pi \cdot \omega(nm)x(nm),$$

or
$$H(nn) - H(mm) = \hbar/2\pi \cdot \omega(nm).$$

This is just Bohr's relation connecting the frequencies with the energy differences.

The quantum condition (11) applied to the previously introduced canonical variables ξ_r, η_r gives

$$\xi_r \eta_r (nn) - \eta_r \xi_r (nn) = i\hbar/2\pi \cdot [\xi_r, \eta_r] = i\hbar/2\pi.$$

This equation combined with (15) shows that

$$\xi_r \eta_r (nn) = -n_r i\hbar/2\pi + \text{const.}$$

It is known physically that an atom has a normal state in which it does not radiate. This is taken account of in the theory by Heisenberg's assumption that all the amplitudes $C(nm)$ having a negative n_r or m_r vanish, or rather do not exist, if we take the normal state to be the one for which every n_r is zero. This makes $\xi_r \eta_r (nn) = 0$ when $n_r = 0$ on account of equation (15). Hence in general

$$\xi_r \eta_r (nn) = -n_r i\hbar/2\pi.$$

If $\xi_r \eta_r = -i/2\pi \cdot J_r$, then $J_r = n_r \hbar$. This is just the ordinary rule for quantising the stationary states, so that in this case the frequencies of the system are the same as those given by Bohr's theory. If $\frac{1}{2}(\xi_r \eta_r + \eta_r \xi_r) = -i/2\pi \cdot J_r$, then $J_r = (n_r + \frac{1}{2})\hbar$. Hence in general in this case, half quantum numbers would have to be used to give the correct frequencies by Bohr's theory.*

Up to the present we have considered only multiply periodic systems. There does not seem to be any reason, however, why the fundamental equations (11) and (12) should not apply as well to non-periodic systems, of which none of the constituent particles go off to infinity, such as a general atom. One would not expect the stationary states of such a system to classify, except perhaps when there are pronounced periodic motions, and so one would have to assign a single number n to each stationary state according to an arbitrary plan. Our quantum variables would still have harmonic components, each related to two n 's, and Heisenberg multiplication could be carried out exactly as before. There would thus be no ambiguity in the interpretation of equations (12) or of the equations of motion.

I would like to express my thanks to Mr. R. H. Fowler, F.R.S., for many valuable suggestions in the writing of this paper.

* In the special case of the Planck oscillator, since the energy is a linear function of J , the frequency would come right in any case.

OBITUARY NOTICES
OF
FELLOWS DECEASED.

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George Peckham

SIR GEORGE BEILBY—1850–1924.

SIR GEORGE BEILBY's life comprised many activities. He was first and foremost a chemical manufacturer and chemical engineer. During the first twenty years of his professional life (1870–90) his work centred on the manufacture of ammonia and oils from the Scottish shales. At the end of this period the introduction of the McArthur-Forrest process for the extraction of gold from its ores by potassium cyanide caused him to transfer his attention mainly to the production of this substance. He invented a process for the manufacture of cyanide from ammonia, which for sixteen years (1890–1906) was worked by the Cassel Gold Extracting Company (now the Cassel Cyanide Company), Glasgow. In 1900, in conjunction with Castner, he invented another process of cyanide manufacture, which involved the use of sodium. In consequence of this he joined in that year the Board of the Castner-Kellner Alkali Company, at Runcorn, who manufactured pure caustic soda. This was the raw material for the manufacture of sodium metal by the electrolysis of the fused caustic. The plant for this he erected at Newcastle-on-Tyne, and for the remainder of his life he was actively concerned with the operations of the works at Runcorn, Newcastle and Glasgow. For more than half a century, therefore, he occupied a foremost place in the manufacture of nitrogen derivatives.

His experience as a manufacturer led him to study the economic utilisation of fuel, and in his presidential address to the Society of Chemical Industry in 1899 he surveyed the various channels of consumption into which the output at that date was flowing. This was the starting point of an inquiry and study which led him to become ultimately the foremost authority on the scientific utilisation of fuel in this country. In 1903 he gave evidence before the Royal Commission on Coal on the output of this mineral and its uses, and made suggestions as to its more economical use. Later he worked for a considerable time on the production of a smokeless fuel for domestic purposes. In 1912–13 he was made a member of the Royal Commission on Fuel and Engines for the Navy. The culmination of his work in this field was his appointment as the first Chairman and Director of the Fuel Research Board in the Department of Scientific and Industrial Research in 1917, a post which gave him the opportunity of putting into practice the conclusions he had formed as to the best methods of utilising scientifically the fuel resources of the country. The war years (1914–18) constituted for him a period of intense activity, and as a member of Lord Fisher's Central Committee of the Board of Invention and Research, and of the Trench and Chemical Warfare Committees of the War Office and the Ministry of Munitions, he rendered services of the utmost value to the country.

The foregoing activities all come under the head of applied science. Successful, however, as Beilby was in all these undertakings, they by no means constituted the whole of his activities. He had an intensely active mind, and one of his recreations took the form of using it keenly in the field of natural philosophy. The conditions of his professional work did not allow him much spare time for these pursuits, and they were always liable to interruption. He chose for his main work the study of matter in the solid state. Primarily his attention was drawn to this by the behaviour of metals when exposed to gases at high temperatures such as he observed in the conditions of manufacturing practice. This work, which could be carried out intermittently and with comparatively simple resources in his own study, was begun with an investigation of the remarkable changes in structure undergone by metals such as iron and copper when exposed to the action of ammonia at from 700° to 800° C., which caused a complete deterioration of their properties. In the first instance, his object was to find a metal or alloy which would be reasonably permanent under such conditions. From this, however, he was led far from the practical problem itself to purely scientific investigations as to the behaviour of metals when subjected to mechanical and thermal treatments of various kinds. These culminated in his well-known theory of the "Hard and Soft States in Metals," which formed the subject-matter of the May Lecture delivered to the Institute of Metals in 1911. No theory has exercised a more profound influence upon the development of physical metallography in the last twenty years, and whatever be its ultimate form, it has fully justified itself by reason of the number and variety of experiments to test its validity to which it has given rise. In this field of investigation Beilby showed himself an acute and skilful inquirer, and nothing illustrates better his intellectual calibre than the fact that though it was essentially "spare-time" work it rapidly became known throughout the scientific world as being of remarkable interest and value. His book on "Aggregation and Flow of Solids"—the only book he ever wrote—represents twenty-one years' work of this kind. It may be regarded as a record of his scientific hobbies, though it by no means exhausts them.

Throughout his life he took a keen interest in organ building, especially in the mechanism, to which he devoted much of his spare time. He erected four organs during his life, and was busily engaged with a fifth for his new home in Hampstead at the time of his death. He did a great deal of the actual work for these instruments with his own hands, and invented a new and ingenious action. The principle was that of tubular pneumatic action, and he employed a high vacuum so as to be able to use the smallest possible tube and pneumatic motor with a view to economy in space, wear and tear. The mechanism for creating the vacuum, though wonderfully conceived and efficient, was too expensive for practical purposes. Playing these organs gave

him great pleasure and refreshment, but the construction was the part which really interested him most.

No survey of his work as a whole should omit a reference to his great services to Education. For many years he lived in Glasgow and interested himself deeply in the work of the Royal Technical College. He was co-opted as a Governor in 1900 and became the Chairman of the Governing Body in 1907. He interested himself in the development of the College on every side. Its finances, buildings, equipment, curricula, and most of all its staff and students, benefited by his wise and generous policy of development. In 1913 the College was affiliated to the University of Glasgow and was included among the institutions recognised for grants by the University Grants Committee. To-day it ranks as a Technological College of very high standing.

Few men have done as much to assist the admission of women to professions, especially the medical profession. This was one of the spheres of work in which Lady Beilby and he have exercised a most beneficent influence. He was one of the Trustees of the Carnegie Trust for the Universities of Scotland, and took the keenest interest in the details of its work. He was a member of the original Executive Committee and General Board of the National Physical Laboratory, which owed much to his generosity and encouragement for many years. He was elected a Fellow of the Royal Society in 1905 and served for several years on its Council.

His scientific work falls under three main heads and is briefly surveyed in the following sections.

A.—THE MANUFACTURE OF SHALE OILS, AMMONIA AND CYANIDE.

The rapid exhaustion of Guano deposits and the increasing consumption of ammonia salts for agricultural purposes so acted on the ammonia market that in the year 1879 the price of the sulphate had risen to £20 a ton. This high price, occurring along with a general fall in the value of several of the commodities produced at the same time or by the same processes as ammonia, formed a powerful stimulant to producers of this substance to increase their output. In 1870 the determination of the nitrogen in Scottish oil shales showed that by the process of distillation then in practice, only one-sixth of the nitrogen was obtained as ammonia. These shales are found below the Coal Measures and are generally associated with marls, limestone and sandstone. They contain a very large percentage of mineral matter, sometimes as much as 80 per cent. When heated to redness in a closed vessel they neither soften nor cake, and the spent shale left after the distillation of the volatile matter still has the outward form of the original substance. Four principal seams or groups of seams are worked in Scotland and Beilby's experiments were carried out at Oakbank on the Broxburn shale. By the process of distillation as practised at that date, the shale was subjected for from 12 to 24 hours to a

low red heat in iron retorts, a current of steam being passed through during the distillation. The distillate from 1 ton of shale consisted of about 30 gallons of crude paraffin oil and from 60 to 80 gallons of ammoniacal liquor. The primary object of the use of steam was to obtain a maximum yield of paraffin products, but it also increased to some extent the yield of ammonia. The Broxburn shale contained 0.72 per cent. of nitrogen, corresponding to 74.8 lbs. of ammonium sulphate in 1 ton of shale. The amount recovered as ammonia in the watery distillate corresponded to only about 12.7 lbs. of ammonium sulphate. The remainder was distributed in the alkaloidal tars and the spent shale.

With a view to increasing the recovery of nitrogen Beilby and Young treated the spent shale to a supplementary steaming after the oil distillation was finished. It was found that by continuing this for several days a considerable proportion of the nitrogen of the shale came off as ammonia. The long period required, however, rendered it commercially inapplicable. They then tried to accelerate the operation by the use of a higher temperature and designed a special retort for this purpose. The steam entered the lower end of the retort and passing through the red hot material became highly superheated and conveyed heat to the raw shale in the upper retort, which was heated by the flue gases passing outside. One of the conditions governing the investigation was that any gain of ammonia which involved a sacrifice of paraffin products was purchased too dearly. The working of the experimental retort, which could deal with 10 cwts. of shale per day, proved very satisfactory. It was found that the double operation of extracting the paraffin oil and recovering the ammonia of the spent shale could be accomplished in from 20 to 24 hours. Further, instead of a lower yield of paraffin products a decided gain was realised. In this way the ammonia output in the watery distillate was raised from 12.7 to 55.0 lbs. of ammonium sulphate. In other words, the yield had been more than quadrupled.

Although this very successful result could be obtained at will in the experimental retort, certain features of the process rendered it improbable that such perfect results could be realised in working on a really large scale. It was noticed that whenever the yield of ammonia rose above 28 lbs. of sulphate per ton, the shale was whitened, due to the burning-off of carbon, and the ash fused. This caused the danger that the fused shale might block the retort and stop its working. Accordingly in the practical working of the shale by the new system, sufficient carbon had to be left in to keep the ash from fusing and this diminished the nitrogen extraction. Following on the experience gained with the experimental unit, a bench of 16 retorts was erected and it was found from its working that a yield of 30 lbs. of ammonia sulphate per ton of shale was all that could be economically won. The general results of working were, however, so satisfactory that the Oakbank Oil Company erected

288 retorts to replace an equivalent number of older retorts, and a gain of about 133 per cent. in ammonium sulphate was realised.

Following on this Beilby and Young devised a new form of retort which was oval and rectangular in cross-section. By this alteration the cubic content of the retorts was increased without a corresponding increase of thickness of the mass of shale to be heated. Moreover, instead of being heated in an ordinary open furnace the retort was heated by a gas producer of novel construction. The new process was introduced in 1881. Beilby estimated that by 1885 the gain in ammonium sulphate output in Scotland was nearly 5,000 tons, which at £10 per ton was equal to nearly £50,000, but in addition there was an increased yield of solid paraffin, valued at about £40,000 per annum. As the costs for labour, fuel and maintenance of the new retorts did not exceed those incurred in the older system of working, the whole of the above saving of nearly £90,000 could be credited to the new process. As a result of their experiments Beilby and Young formulated (Patent No. 1377 of 1882) the conditions for the successful conversion of the nitrogen of carbonaceous residues into ammonia, these being that the coke or residue should be burned in steam alone or in a mixture of steam and air, sufficient excess of steam being present to protect and carry off the ammonia as formed. The temperature while sufficient for the combustion had to be below the fusing point of the mineral ash. Beilby's later work in this field was concerned with the heating of his retorts by a suitable form of producer-gas. This contained from 60 to 70 per cent. of the heat energy of the coal from which it was produced, and in this case the ammonia varied from 80 to 130 lbs. of sulphate per ton of coal. The development of producers of this type involved continuous work in gradually overcoming the weak points of structure or working.

The principle of Beilby's process for the manufacture of cyanides was the passage of a current of ammonia over or through a mixture of alkaline carbonate with alkaline cyanide and finely divided carbon at a temperature sufficiently high to keep the mixture fluid and to decompose the ammonia. By this means carbon and ammonia were consumed and a large part of the carbonate converted into cyanide. The fused cyanide obtained was contaminated with a small percentage of finely divided carbon, which was removed by settling or filtration. One of the important conditions for success was so to adjust the proportions of the several ingredients that the mixture was fluid at a temperature below that at which the containing vessel, consisting of iron, would be rapidly destroyed. As the result of numerous experiments, Beilby found that a mixture of from 55 to 60 per cent. of potassium carbonate, 20 to 25 per cent. of carbon, and 20 per cent. of potassium cyanide fulfilled these conditions best. With such a mixture it was found possible to carry out this process with the minimum wastage of materials and damage to the apparatus. The process could be carried out in one of two ways :—

In the one, the reaction vessel was an iron pot provided with an inlet pipe for ammonia, an outlet pipe for the gases evolved in the process, an opening or hopper for the introduction of the solid materials, and a tap-hole for running off of the finished cyanide. When the mixture was thoroughly fused, ammonia was bubbled through it. Throughout the operation it was important to have a sufficient proportion of cyanide to render the mixture thoroughly fluid. As the reaction proceeded the mixture became more fluid by the formation of further quantities of cyanide, and fresh quantities of carbonate and carbon were added from time to time until the pot was filled to its fullest working capacity. The supply of ammonia was then kept up till the desired proportion of cyanide was obtained, after which the fused salt was settled or filtered and run into moulds or drums. The evolved gases containing some undecomposed ammonia were either led through successive melting-pots or absorbers for the recovery of ammonia.

In the other process the production of cyanides was carried out in a more continuous manner in vertical retorts kept at a suitable temperature by an arrangement of furnaces and flues. The bottom of the retort was closed and formed a melting pot in which the cyanide collected, and from which it was periodically run off. The lower part of the body was fitted with perforated shelves, and ammonia was led into this part. A central revolving shaft carried discs or arms which stirred and swept the mixture on to the shelves and caused it to drop from shelf to shelf. The mixture of carbonate and carbon with or without cyanide, according to circumstances, was fed through a suitable hopper at the top of the retort on to the top shelf, where it was acted on by ammonia with the formation of some cyanide, which made it fuse and drop to the next shelf. The revolving arms prevented the imperfectly fused mixture on the top shelves from frothing up in a dangerous manner, and mixed and drove forward the reaction products. The retorts were provided at their upper ends with exhaust pipes for the gases, which were dealt with in the same way as those evolved from the melting pots. Beilby found that not only could he use carbon in the form of charcoal, lamp-black, coke, etc., but that by using pitch from the basic tars of crude shale, coal oil or peat tar, he was able to recover a large part of the nitrogen as cyanide. Moreover, as a substitute for ammonia he could use the volatile bases from shale oils, peat tar, or from animal or bone oil.

A difficulty, however, which he was never able to overcome, and which, no doubt, weighed with him in abandoning this process and substituting that devised by him in conjunction with Castner, was the impossibility of finding any metal tube which would withstand for more than a short period the action of ammonia at the temperatures used in the process, and, in conjunction with Professor G. G. Henderson, he carried out an investigation on the nature of these changes.

Their main conclusions were that metals in general, when exposed to the action of ammonia at high temperatures, were either converted into nitrides wholly or in part, or else profoundly changed in their physical properties, even although no nitrogen was permanently fixed by the metal. In every case marked disintegration occurred, due, in their view, to the continuous formation and decomposition of unstable nitrides. They examined the corroded metals under the microscope and observed a characteristically spongy structure, due to the escape of innumerable minute gas bubbles from a molten or pasty mass. In the case of copper, it appeared that the reaction began by the ammonia molecules attacking the surface molecules of the metal and forming a fusible nitride. With sufficient excess of ammonia a theoretical absorption of nitrogen would, no doubt, take place, but the nitride, being fusible at the temperature of formation, penetrated into the copper, and further action took place at some distance from the surface, where the ammonia molecules were fewer and the hydrogen molecules relatively more numerous. At a certain distance from the surface they concluded that a point was reached at which the ammonia and hydrogen molecules balanced each other so exactly that either no nitrogen was absorbed or as soon as a molecule of nitride was formed it was decomposed with evolution of nitrogen. In either case the hydrogen resulting from the decomposition of the ammonia, together with the nitrogen from the decomposition of the nitride, forced their way to the surface of the fluid nitride and caused the appearance of boiling—the peculiar structure found in all metals which have been acted on by ammonia.

B.—STRUCTURE, AGGREGATION AND FLOW OF SOLIDS.

Beilby's striking and beautiful work in this field arose directly out of the previous investigations. He took up the study of the structure of solids, and in particular of metals and their behaviour under various forms of mechanical deformation and thermal treatment. He devoted, in the first instance, much time to an investigation of the operations of cutting, filing, grinding and polishing the surface of solids, and concluded that in all cases a thin film was formed which was in many respects essentially different from the general body underneath it. He concluded that this film resulted from a certain mobility conferred on a thin layer of molecules by the tool or polishing agent moving over the surface, and that while in this mobile condition the film of solid molecules behaves like a liquid and is subject to the action of surface tension. Many of his early experiments were carried out with calcite, a mineral which, owing to its characteristic cleavage fractures, enabled him to start with a level surface upon which no mechanical work had been done. It was also a substance which lent itself peculiarly well to study under the microscope.

He found that the polished surface of such a cleavage plate, even when

illuminated by an intense beam, showed no trace of the disturbance to which it had been subjected by the operation of polishing, but by adopting the method of removing step by step the surface layers by a solvent, he was able to investigate the nature and extent of the action. His conclusion was that the lamellæ had been ploughed and broken up to a depth of from 500 to 1,000 $\mu\mu$. The complete obliteration of the traces of this disturbance led him to conclude that, as it passed through the mobile to the solidified state, the disturbed substance must have extended through the whole depth of the affected layers, otherwise the healing of the deeper furrows would have been imperfect and their traces would have been shown by the oblique beam. The laying bare of the disturbed layers by the action of the solvent showed that this action was selective and that the substance which had been flowed and solidified was first attacked. (He drew similar conclusions from polished surfaces of rock-crystal, and concluded that the molecular arrangement of the flowed substance must be different from that of the original crystal.) He found further that the surface layer formed on calcite by polishing was harder than the unaltered crystal surface, and that it was equally hard in all directions which the natural surface is not. The new surface formed a genuine protecting skin over the crystal surface. The essential feature of polishing, therefore, in his view, was the production of a true skin of vitreous material. In this respect it differed essentially from grinding, cutting, filing or any other form of mechanical deformation. This discovery opened up for him a new field of study on the crystalline and vitreous (flowed) states of matter, and in following it up he made a number of experimental observations which led him to originate and expound a new theory of the hardening of metals by plastic flow during cold working.

According to this, hardening results from the formation, at all the internal surfaces of slip or shear, of mobile layers similar to those produced at the outer surfaces of the metal by polishing. These layers he conceived to retain their mobility only for a very brief period, and then to solidify in a vitreous state, thus forming a cementing material at all surfaces of slip and shear throughout the mass. He regarded the physical and other properties of the two states in metals as not merely distinct, but obtained evidence of the existence of a definite stability point and argued from this that not only must all crystalline substances be capable of existing in the vitreous state, but that it is possible by purely mechanical means to transform them into it. He made numerous experiments to convert a metal completely from the crystalline into the vitreous condition, but never succeeded in doing this. He found that no matter what form of mechanical work he employed, the final result was a composite structure, consisting of a mixture of crystalline (soft) and vitreous (hard) material. Moreover, he concluded that the rigidity and tenacity of the work-hardened metal depended quite as much on the "texture" or type

of structure developed as on the actual proportions in which the two states were present. According to his theory, therefore, the crystalline state of any metal while stable thermally was unstable mechanically.

The vitreous (work-hardened) state could, he concluded, be reconverted into the crystalline state by appropriate heat treatment. This temperature was in most cases quite low, *e.g.*, in the case of gold, silver and copper it ranged between about 225° and 275° C.—in all cases several hundred degrees below their melting point. These transition temperatures he investigated by a variety of methods, *e.g.*, recrystallisation, loss of mechanical stability, development of thermal E.M.F. between the wires in the hard and soft states, and the restoration of elasticity as judged by accoustical properties. He obtained concordant results by these methods and concluded that they pointed to the occurrence of a true change of state in the hardened metal when a certain temperature was reached, this change being the development of the crystalline from the vitreous condition. The vitreous state, therefore, while mechanically stable was thermally unstable.

On annealing, no important softening of the metal or reduction of its mechanical stability occurred till the recrystallisation range of temperature was reached, but at this point there was a sharp drop in the stability curve, which continued as the temperature of annealing was raised over a range of about 50°. Throughout this, a corresponding growth of the crystalline grains occurred.

Beilby found that the thermal E.M.F. was an exceedingly delicate indicator of the state of strain in hardened wires, and regarded the observed values as due in part to strains of a temporary character, and in part to a physical change of state of a fundamental nature. The secular changes in hardened metal, which were not completely eliminated until about 200° C., he regarded as limited to the gradual relief of strains similar in kind to the contraction strains observed by Muir in the case of glass-hard steel. This relief of strain differed not merely in degree, but also in kind from the molecular change which occurs when the crystallisation temperature is reached and complete re-orientation of the molecules takes place. The first state is unstable even at ordinary temperatures, while the second is stable up to the lower limit of the crystallisation range. The first stage in the relief of strain is not accompanied by any change of microstructure, while in the second a very obvious change occurs. Beilby suggested that in the first state the molecules themselves are strained, while in the second state they are merely restrained by their mutual cohesion from turning into a uniformly-oriented condition.

One of the essential facts which emerged from the foregoing studies was that the molecules of a pure substance can be assembled in aggregates which possess widely-different degrees of mobility in response to heat or mechanical disturbance. The contrasted qualities of hardness and softness, of rigidity

and mobility must, therefore, be intimately associated with the ultimate molecular structure of the aggregate. In the vitreous state, where the molecules are in a condition of elastic strain, Beilby regarded the energy stored in the molecules as in a collection of coiled springs.

Based on the researches thus summarised, he put forward the hypothesis of "Molecular Pulsation Cells." The molecule, which for simplicity he took as monatomic and spherical, is regarded as elastic and capable of responding to ether-borne vibrations of a period proper to itself and of an amplitude proper to the temperature attained. Its elasticity was assumed to be that of volume and the vibrations of the spherical molecule were assumed to be spherical pulses. According to the hypothesis the effect of these pulses, the period of which is enormously rapid, is to surround the sphere with a "pulsation cell," the thickness of which will depend on the amplitude of the pulsations. This, in its turn, depends on the temperature, so that for each temperature the cell is of definite thickness.

When an aggregate of spheres at the absolute zero is energised by heat, each molecule surrounds itself with a pulsation cell proper to the temperature which it has reached, and the molecules are pushed apart to a corresponding distance. The outer surface of the cell, though itself purely kinetic in its origin, forms in certain respects a perfectly real bounding surface and not merely a vague sphere of influence. This well-defined surface marks off the space occupied by the molecules just as effectively as a rigid static boundary would do. According to this hypothesis, the mutual cohesion of the molecules is weakened by heat, because the molecular bounding surfaces are so enlarged by their pulsation cells that they are gradually pushed further and further out, till the cohesive force per unit of surface is reduced to a negligible quantity. When this stage is reached, the molecules are no longer held together by their mutual attraction; they are free to fly apart in the gaseous state. Even in this state, however, Beilby regarded the bounding surface of the pulsating cell as real, and as effective as in the molecules in the solid state of aggregation. In this case the molecular encounters in the gaseous state will take place at the bounding surfaces of the pulsation cells and not at the original surfaces of the molecules. In this way, the energy of the pulsation of the gas molecules is regarded as the original source of the kinetic energy from which the translational and rotational forms are naturally derived during the encounters of the pulsating molecules.

In a collection of molecules under the influence of cohesion alone the packing tends to be entirely haphazard, for the spheres stick to each other at the points at which they first touch and can only be moved into new positions by externally applied force. The packing is not the closest possible; on the contrary, it can be extremely open; neither is it homogeneous. While the molecules in an assemblage of spheres of this description have no powers of self-arrange-

ment, it is evident that the development of pulsation cells introduces a new set of conditions, all of which make generally for an increase of mobility or a reduction of rigidity in the assemblage. Certain of these conditions Beilby regarded as tending to the development of power of self-arrangement among molecules. While this latter power would probably be at a minimum in spherical molecules vibrating with spherical pulses, it would become a very powerful influence if the pulses were equatorial or polar, for then the spherical molecules would develop around these oblate or prolate spheroidal cells. Kinetic cells of these forms would probably tend to arrange themselves in some simple and homogeneous mode of assemblage. This kind of assemblage is the really essential feature of the crystalline state. In this way the pulsation-cell hypothesis enabled him to visualise to some extent the advent of the automatic power of crystallisation in the molecules as they are energised by heat.

It is evident that the hypothesis is capable of considerable development, not only in this but in other directions. When it is applied to the case of complex molecules consisting of two or more atoms of the same kind, or to compound molecules containing atoms of different kinds, it becomes possible to picture a great variety of forms which the compound pulsation cells might assume, and the changes in these forms which would result at different temperatures. The latter point is of special importance, because it may supply the physical explanation of the different crystalline phases of the same substance which are only stable over a certain temperature range, *e.g.*, the rhombic and prismatic forms of sulphur. If it is accepted that crystallisation results from efforts of the pulsating molecular cells to reach certain positions of equilibrium, it follows that their displacement from these positions by mechanical disturbance and flow will leave the assemblage in the non-crystalline or vitreous state, unless the substance is at or above the temperature at which the cells are sufficiently developed to ensure their automatic return to the crystalline forms.

Beilby's hypothesis of the crystalline and vitreous states of metals was widely accepted by English and American workers, and, as previously mentioned, has given rise to much further experimental work designed to test its validity. It was, however, never accepted to the same extent by Continental workers. It has the merit of explaining in a simple and rational manner a large number of well-established facts with reference to metals and alloys in the work-hardened and heat-softened conditions. Some workers, however, have always felt doubtful whether the crystalline state was as mechanically unstable as Beilby supposed, and their scepticism appears justified in the light of the experimental evidence obtained by the application of X-ray analysis to the study of metals in the work-hardened condition. According to this, it appears as though even very severe mechanical work, such as wire-drawing, does not actually render the metal non-crystalline, but tends to cause the crystals

to assume a uniform orientation of a particular kind. This is certainly the case with such severely worked materials as drawn tungsten wire and beaten gold-leaf. It may be, therefore, that Beilby's hypothesis of the *vitreous* condition of metals will have to be modified. He himself would have been the first to agree to this on the production of adequate evidence. Whatever form, however, the theory finally takes, the beautiful experimental work upon which it was founded remains unshaken.

C.—THE UTILISATION OF FUEL AND THE PRODUCTION OF POWER.

In his Presidential address to the Society of Chemical Industry in 1899, Beilby collected figures and statistics from all sources as to the various channels of consumption into which the yearly output of 200 million tons of coal in this country was flowing. His inquiry extended over about three years and gave the following results:—Of the 157 million tons consumed at home, 76 million tons were used for the production of power for industrial purposes, 46 million for the production of heat for industrial purposes, and 35 million for the production of heat for domestic purposes. Two and a half years later the Government appointed a Royal Commission with powers of inquiry into the position of the national resources in coal. This inquiry included in its scope the question of the saving in these resources which might be made through the adoption of more economical methods of consumption. At the request of the Commission, Beilby revised the foregoing estimates and presented them in a somewhat more detailed form. He then gave the following figures:—

Coal Consumption.

	Tons.
Railways	13,000,000
Coasting steamers (bunkers)	2,000,000
Factories	53,000,000
Mines	18,000,000
Iron and steel industries	28,000,000
Other metals and minerals	1,000,000
Brick works, potteries, glass works, and chemical works	5,000,000
Gas works	15,000,000
Domestic	32,000,000
	167,000,000

In 1906 he carried the matter still further in a paper on "Modern Power Production and its Relation to the Coal Resources of Great Britain." This paper contains a most careful study of the cost of the production of electrical power in this country. He showed that the total cost of producing one E.H.P. continuously for one year was £4 6s. 8d. at a central generating station

in the north of England. Against this the cost of power at Niagara Falls was from £4 to £5 per E.H.P. year, while at the Rhine Station in Baden it was from £5 to £7. This showed that the coal resources of Great Britain placed its manufacturers in a very favourable position as users of power, even when compared with that of foreign manufacturers who had the good fortune to be located in the neighbourhood of the leading water-power stations of the world. He concluded that a saving of 40 million tons might be effected at that period on our national coal bill for power production.

The first part of the paper deals with the enormous waste in producing power from coal by burning it under small steam boilers, while the second part surveys the particular fields of usefulness of the gas engine and the steam turbine. He took the position that, from the standpoint of thermodynamic efficiency, the combination of the gas producer and gas-engine must take a higher place than any combination of steam boiler is ever likely to do. With these it had been proved possible to obtain 30 per cent. of the heat value of the fuel as useful work, and a figure of coal consumption of 1 lb. of bituminous slack per 1 h.p. had been again and again confirmed. Moreover, from the thermodynamic standpoint the internal-combustion engine must from its nature have much greater potentialities than the steam engine can ever have. The question, however, is different when engines are compared from the practical point of view, as machines which have to be steadily worked and maintained at a certain pitch of excellence for long periods of working life. It is here that the advantage is with the steam turbine. The practical difficulties of the gas-engine maker may be traced to the necessity which has arisen over larger units of power. There is no difficulty about engines up to 100 h.p., but with the necessity for much larger cylinders and moving parts the problem of practical construction becomes increasingly serious. The mere alteration of the ratio of the capacity of the cylinder to its surface brought about by the increase of size, brings with it a number of problems which have practically to be solved afresh with every step upwards in the dimensions. These relate to the distribution of heat and to local overheating of the metal with the production of severe and sometimes disastrous strains. The uniform mixing of the much larger volumes of gas and air, which have to be drawn into the cylinder in a fraction of a second and ignited with certainty at the exact moment when the crank has reached the proper point, is in itself no small problem. Any trifling acceleration in the ignition period may wreck the engine, while any retardation in that rate must lower the efficiency. The wear of the hot surfaces within the cylinder and the risks of erosion by streams of intensely hot gas further add to the complexity of the problem.

Against this the steam turbine had already passed out into the field of practical engineering in just those departments where the conditions of power production are most exacting. The influence of the turbine has made itself

felt in modern propulsion and in the production of power in central stations, two situations in which the responsible engineer must only employ means which have stood the severest tests under prolonged running. The cost of power production by steam turbines necessarily depends on local conditions. Cheap coal, easy disposal of ashes, good feed-water for the boilers, an ample supply of clean cold water for the condensers, are all necessary if the minimum cost of production is to be maintained. Large units must be employed to keep the loading fairly regular. Given these conditions Beilby concluded that the cost of production could be maintained in regular working at from £4 to £5·per E.H.P. year of 8,760 hours. This is substantially the same as the gas-engine figure.

From this comparison his verdict was that while the steam turbine offers great advantages for power production on a large scale in suitable localities, the gas-engine offers its own special advantages, for an equally low cost of production may be maintained from a much smaller installation, while it can be worked with economy in almost any situation where coal could be obtained at a reasonable price.

In a contribution to the discussion on Fuel Economy, held in Section B. of the British Association at the Birmingham Meeting of 1913, Beilby considered the application of destructive distillation to raw coal as a means of promoting economy, efficiency and cleanliness, with especial reference to Low Temperature Carbonisation. The industrial applications of destructive distillation are most naturally classed under three principal divisions, according to the primary product which it is desired to obtain. In the first of these hard coke is the primary product, in the second illuminating gas, and in the third paraffin wax and oils. In each case secondary products result from the distillation, but in spite of their increasing importance in each division of the industry, the primary product is and must continue to be of paramount importance. In his selection of raw materials the gas maker has probably the greatest freedom of choice, for illuminating gas can be made from almost any variety of coal. The choice of the coke maker is more restricted, for he can only use caking coals which will yield a hard and compact form of coke. The choice of the oil maker is even more restricted. For him the oil shales of Mid and West Lothian supply the only suitable material. In each of these divisions of industry the primary product is being produced to supply the demands of markets which already exist. If an important revolution in any division of the industry is contemplated Beilby pointed out that its effect on these existing markets must be carefully considered.

He estimated that out of a total home consumption of 180 million tons at that time, not more than 35 million tons is distilled in retorts, ovens and gas producers. "Is there," he asked, "any further proportion of this huge total which, in the light of the best knowledge of to-day, ought to be subjected to

preliminary treatment by distillation before it is used for heating purposes." With regard to the 35 million tons used for domestic heating, Beilby reviewed the possibilities of the process introduced by Parker for making Coalite, a smokeless domestic fuel made by the distillation of coal at a temperature of 400° to 450° C., in contrast to the gas-retort method of distillation at 900° to $1,000^{\circ}$ C. This paper by Beilby describes experiments in which the coal could be exposed to the action of heat in thin layers. The first practical apparatus consisted of a column heated externally in a gas-fired oven and fitted internally with a series of sloping shelves. Mechanical arrangements were made for feeding the small coal into the top of the column, and for mechanically jolting the shelves so that the coal passed over the whole series from top to bottom in a sheet 2 to $2\frac{1}{2}$ inches in thickness. The coke was mechanically withdrawn from the bottom of the column, and the volatile products of distillation removed by an exit pipe to suitable condensers and receivers. It was found that this coal could be exhausted of its gas at from 400° to 450° C. in not more than $1\frac{1}{2}$ hours. In Parker's apparatus, where the coal had been heated in small vertical tubes, the time taken was four hours, and even then it was doubtful if the distillation was complete in the centre. Beilby constructed a unit of his apparatus with the capacity of 15 tons per day. He satisfied himself that the principle of exposing coal to heat in thin layers is sound ; it would, however, only work smoothly with non-caking coal. Caking coal was apt to stick to the shelves and accumulate on them. The coke made in this way was burnt in producers, and proved satisfactory for the making of water gas. Some of it also was converted into briquettes for domestic fuel, and these proved satisfactory. The thermal value of the hydro-carbon gases reached the high figure of 850 B.T.U. per cubic foot. Attention, however, was mainly concentrated on the mechanical development of this method of distillation and on the production of a domestic or an industrial fuel from the coke. Beilby concluded that the apparatus must be in fairly large units, must be automatic, and work with the smoothness and regularity of the best types of automatic stoking machinery and with the minimum of manual labour and detailed supervision.

His last public utterance on the scientific utilisation of fuel was the James-Forrest Lecture, delivered in 1921, entitled "Fuel Problems of the Future." In this lecture Beilby paid special attention to the remarkably rapid development in the winning and use of brown coal and lignite in Europe, and particularly in Germany. He pointed out that in 1920 the total production was 140.7 million tons, to which Germany contributed 111.6. Though in its natural state a less concentrated fuel than bituminous or anthracitic coal, brown coal has many points in its favour. The chief of these is the low cost at which it can be won as compared with ordinary coal, and where extensive depths of great thickness occur, these can be open-cast and excavated by machinery. The manual labour required is much smaller in amount for a

given output and is of a less highly specialized type, while the special dangers and uncertainties of coal mining are practically absent. Capital charges are relatively light, and, though it contains from 40 to 60 per cent. of water, it is to-day by far the cheapest source of thermal units. Its further manufacture by drying, briquetting and carbonization, can be carried out close to the point of excavation and under conditions favourable to production on a large scale, and therefore at a low cost.

The main conclusions reached in this lecture, which covered an extremely broad survey of available fuels, were as follows :—

1. That coal is likely to remain for a long time the world's chief source of fuel, but that its more efficient use may be secured :—

(a) By more careful sorting and preparation at the mine.

(b) By the improvement of boiler firing on well-known lines.

(c) By the sorting out of its combustible constituents into fuels of higher availability or convenience.

(d) By preliminary carbonization carried out either at high or at low temperatures.

This has an important bearing on the development of home sources of fuel oil and motor spirit, and on the production of smokeless solid fuel for domestic purposes.

2. The development of oil shales as a source of liquid fuel is still only in its initial stages, but evidently has a great future before it.

3. The problems of the utilization of peat, which cover a wide range, both technical and chemical, are mainly of local importance, and are not likely to affect the fuel supplies of the world to any great extent.

4. The production of alcohol on a really large scale, as a motor fuel of high availability, bristles with chemical and technical difficulties, and it is still too soon to pronounce an opinion on the possibilities of the future.

Beilby was careful to state, however, that the most difficult of the fuel problems of the future are those into which the human element enters so largely. He pointed out that, at home, the relations of the wage-earning classes with the actual leaders who initiate and direct our industrial policy, and abroad, our relations with other nations who are equally interested with ourselves in the national resources of the world, are profoundly affected by the spirit of the times. This spirit as it is manifesting itself to-day is fatal to the progress of reconstruction and development on any extensive scale, and he concluded :—“ We, whose chief interest in life lies in the control and use of the powers and resources of nature for the service of man, can only continue to do the work next our hand, while we cherish the hope that the better side of human nature, which we know is only temporarily over-shadowed, will gradually reassert itself.”

The culmination of Beilby's work on fuel was his appointment by the Lord

President of the Council to the Chairmanship of the Fuel Research Board and the Directorship of Fuel Research—posts created for him. The research station was erected at East Greenwich. It was designed, constructed, and equipped under his close personal supervision, and embodies his conception of a centre of national research on the scientific utilization of fuel. This post he held for six years, and the record of the programme of work and experiments carried out is contained in the “Reports of the Fuel Research Board,” issued annually under the general auspices of the Department of Scientific and Industrial Research.

Beilby concerned himself mainly with two investigations: (1) a survey of the properties of the various coals (including brown coals) mined in the British Isles and the Irish Free State, with a view to their more scientific utilization; and (2) methods of rendering Great Britain as far as possible self-supporting in the matter of fuel oils, from the point of view particularly of the requirements of the Navy. With reference to the latter, the Royal Commission on Fuel and Engines for the Navy, 1912–13, had reported that the only means of securing this end lay in the development of a new carbonizing industry, founded on the distillation of coal at a temperature much below that used in gas retorts or coke ovens. This was actually the first problem attacked by him. The war was still in progress, and the urgency of its solution was obvious. Within a year it had been sufficiently solved in its scientific and technical aspects to enable an adequate supply of oil fuel to be produced if the need had continued to press; but with the low-temperature distillation method employed coke is still the main product of the process, and its commercial disposal still remains a problem. A by-product of his activities at the Board was the establishment of the “therm” as the basis for the charging of town gas to consumers.

A study of Beilby's life and work as a whole leaves a vivid impression of his greatness. He was a successful manufacturer and an acute and patient scientific investigator. Though he gave the impression of alertness and quickness of thought, his mind really preferred to work slowly and cautiously. It was speculative, but always scientifically controlled. It was this quality which gave his scientific work its peculiar value. He was also a great public servant and citizen. He possessed great nobility of character and endeared himself by his personal qualities to his friends. He had in a pre-eminent degree the quality of charm, and this was felt not merely by his intimate friends but by those who met him, perhaps, only a few times. He carried in his face a look of rare high-mindedness and elevation. Probably no one will ever know the full extent of his generosity, for it was always exercised in the quietest possible way, and it is doubtful whether anyone has ever helped so many other investigators, whatever their age, or helped them in a more perfect way.

H. C. H. C.

SIR THOMAS EDWARD THORPE—1845–1925.

By the passing away of SIR EDWARD THORPE on February 23 last, at his Devonshire home by the sea, Whinfield, Salcombe, British chemistry lost one of its chief exponents, and chemical research one of the outstanding figures of the last fifty years, a period of the most remarkable progress ever made in experimental science. He had been ailing more or less seriously ever since the Edinburgh meeting of the British Association in 1921, at which he was President, but, to everybody's regret, was unable to deliver his address in person owing to sudden indisposition; yet he had latterly shown so much of his old energy that it came almost as a surprise when his death was announced. In the summer of 1923, for instance, he was quite remarkably active as a Vice-President of the Devonshire Association, who held their three days' annual meeting that July at Salcombe, under the presidency of the writer, who stayed at Whinfield as the guest of Sir Edward and Lady Thorpe. The revision of his 'Dictionary of Applied Chemistry,' for the new edition, was at that time occupying his attention very closely.

Thomas Edward Thorpe was born on December 8, 1845, at Barnes Green, Harpurhey, near Manchester, his father, Mr. George Thorpe, being a Manchester merchant engaged in the cotton trade. He was educated at the Hulme Grammar School, and subsequently at the Owens College, now Manchester University. Here he came under the notice of Prof., afterwards Sir Henry, Roscoe, to whom he became research assistant, being associated with him in the well-known photo-chemical investigations and those concerning vanadium, the atomic weight of which he determined, with (at last) pure material, and the dichloride of which he discovered.

On the completion of these early investigations Thorpe went to Heidelberg to study under Bunsen, and there took the degree of Ph.D. Subsequently he migrated to Bonn, and studied under Kekulé, with whom he published in 1869 a paper on ethylbenzoic acid. His first work under Bunsen at Heidelberg was determined by a somewhat remarkable incident. Prof. Roscoe was himself an old pupil of Bunsen, and sent by his young friend Thorpe a present to the great chemist, consisting of some very fine crystals of the alkali metals, sodium and potassium, contained under rock oil in two separate bottles. To economise luggage space, however, Thorpe conceived the bright idea of concentrating both sets of crystals, which were fairly easily distinguishable, in one bottle, and at his first interview presented the bottle, neatly wrapped up, to Bunsen. But, alas, when the cover was removed no crystals were to be seen, but instead only a liquid like tarnished quicksilver, beneath the rock oil. The moment was an embarrassing one for both parties, but Bunsen quickly relieved the situation



F. S. Florky

with a smile, and the recommendation to his new research student to devote his first research at Heidelberg to discovering the nature of this extraordinary liquid. It turned out to be, of course, the now well-known liquid alloy of the two alkali metals.

While at Heidelberg Thorpe had the good fortune to have as companions, both in the laboratory and in lodging apartments, Victor Meyer and his brother, which accounts for the great friendship which Victor always showed for Thorpe on his visits to England. Those must have been lively days in the German universities, for the writer well remembers Sir Edward relating how another of their fellow-lodger students was killed in a sword duel, the usual everyday sword play in the "Commers" having been carried to extremes at an outdoor early-morning rendezvous.

After some further photo-chemical work in collaboration with Roscoe, resulting in two joint papers published in 1870, Thorpe was elected in that same year to the Professorship of Chemistry in the Andersonian College of Glasgow. This year, 1870, was also notable in his career for his marriage to Miss Caroline Emma Watts, the daughter of Dr. John Watts, one of the most highly respected of the group of great men who made Manchester what it is to-day, and who did invaluable work as Chairman of the Manchester School Board and the Union of Lancashire and Cheshire Institutes. Dr. Watts proved a very kind friend to the writer when leaving the tuition of Prof. Roscoe at the Owens College to take up a Royal Exhibition at South Kensington in 1883, and it was to this, and the introduction it gave to Dr. Thorpe, that the writer's long association with the late Sir Edward was largely due. It need scarcely be mentioned—the fact is so well known—that Lady Thorpe proved a splendid helpmate, and her husband's life-work must have been most happily facilitated by the well-ordered home life with which she so devotedly surrounded him.

During his occupancy of the Chair of Chemistry at Glasgow Thorpe published, besides several papers of lesser importance, four memoirs concerning respectively a new oxychloride of chromium, the chlorides of phosphorus, the constitution of paraffin, and the interaction of phosphorus pentasulphide and carbon tetrachloride. He also made a contribution to the observations (being responsible for those on chemical light intensity) of the solar eclipse of December 22, 1870, in Sicily, an expedition which had the misfortune to be shipwrecked in H.M.S. *Psyche* off Aci Reale on December 15, on the passage from Naples to Sicily.

In 1874 Thorpe was elected to the Professorship of Chemistry in the Yorkshire College of Science, Leeds, then lately established, and now the University, a post which he occupied for eleven years. During this period he carried out a brilliant series of researches on the specific volumes of liquids of definitely related chemical constitution, in which his special ability in delicate manipulation, for which he had a remarkably small and delicate hand, and determination to arrive at the highest accuracy were especially brought out. New

methods of determining the density and thermal expansion of liquids were devised, which have proved of standard value, and the results were so important that in 1876 he was elected a Fellow of the Royal Society. He also published a particularly interesting paper on the specific volume of water of crystallisation in collaboration with J. I. Watts, Lady Thorpe's youngest and now only surviving brother. Moreover, he collaborated during this period with his colleague Prof., afterwards Sir Arthur, Rücker of the physics department, in several researches in physical chemistry. In 1878 he formed a member of the party who went out to La Junta, Colorado, to observe the solar eclipse of July in that year. Before returning he carried out, jointly with Prof., afterwards Sir Arthur, Schuster a series of magnetic observations along the fortieth parallel, between the Atlantic and the Great Salt Lake. Next, he carried out in 1880 magnetic observations at the Azores, and in 1883 published a paper, conjointly with Sir Arthur Rücker, on the irregularities of magnetic inclination on the west coast of Scotland. These papers contained the preliminaries to a systematic magnetic survey of the British Isles in collaboration with Sir Arthur Rücker, which commenced in 1884, formed the subject of the Bakerian Lecture of 1889, and was extended further subsequently to include 205 stations, the final results forming the subject of a paper which occupied the whole of volume 188, year 1896, of Series A of the 'Philosophical Transactions.' The writer can speak with inner knowledge of the magnitude of this work, as he made the computations and maps for the first part of the survey described in the Bakerian Lecture and trained the staff who carried on the work for the subsequent extension.

In 1885 came the call to succeed Sir Edward Frankland at the Normal School of Science and Royal School of Mines at South Kensington, afterwards known as the Royal College of Science, and now the Imperial College of Science and Technology. It was a popular appointment with us students there, as the research fame of Prof. Thorpe had gone before him. The writer, then in his third year as a Royal Exhibitioner, was from the first, owing to the kind introduction of Dr. Watts, the new professor's father-in-law, set to work on original investigation, the subject being the oxides of phosphorus, a research which lasted some years, during which the writer became assistant demonstrator and then demonstrator and lecturer in chemistry. The main object was to investigate the statements then current in text-books concerning the supposed lower oxide, P_2O_3 . It was assumed to be a white powdery substance resembling phosphoric oxide, but this turned out to be so grotesquely inaccurate that it became obvious that phosphorous oxide had never been isolated. For some time this oxide eluded us, but we were in the meantime rewarded by the discovery of the tetroxide, P_2O_4 , which was isolated in good crystals, and described to the Chemical Society in 1886. Eventually phosphorous oxide was isolated, and proved to be a very volatile substance, white, waxy, and compact

when condensed in quantity, but forming arborescent crystal aggregates when condensed in small quantity, and magnificent large highly refractive (affording brilliant spectrum colours) single crystals when re-sublimed *in vacuo* or in an inert gas, all of which forms melted readily at 22° C., so that on a summer's day the substance is a liquid. When heated in an inert atmosphere it boils practically undecomposed at 173° , and its vapour density was consequently obtained without difficulty and found to correspond to the double formula P_4O_6 .

Two joint papers, by Sir Edward and the writer, describing it and its reactions and additive compounds were communicated to the Chemical Society in 1890 and 1891, and a further paper on its compound with sulphur, $P_4O_6S_4$, formed the first article of the new publication, the '*Zeitschrift für anorganische Chemie*.' In preparing this substance some violent explosions occurred, in one of which the Professor was knocked down, but fortunately was unhurt. The discovery of phosphorous oxide had one very pleasing result, for Sir Lauder Brunton, who most kindly investigated for us its physiological effect, found it to be the cause of the terrible jaw necrosis from which so many of the workers in match manufactories suffered. We were able to indicate how to avoid its formation in match-making by the use of red phosphorus instead of yellow, for it is only the yellow which gives rise to it on oxidation, the temperature of oxidation of red phosphorus being too high and the product being phosphoric oxide. The disease has consequently been banished from the match-making industry.

During this South Kensington period Thorpe carried out, in collaboration with Sir William Abney, our Director for Science at the Department of Science and Art, observations of the solar eclipse at Hog Island, Grenada, West Indies, on August 28-29, 1886, and at Fundium, French Senegal, on April 16, 1893, as regards the photometric intensity of light. He also determined the atomic weights of titanium (commenced at Leeds), silicon (with J. W. Young), and gold (with A. P. Laurie), carried out experiments on coal-dust explosions in mines (also continued from Leeds), and on the decomposition of carbon disulphide by shock. He further carried out an exhaustive examination of the celebrated waters of Cheltenham. In collaboration with F. J. Hambly he published a paper on manganese trioxide, another on phosphoryl trifluoride, and a third on the vapour density of hydrogen fluoride. With W. Kirman he described fluosulphonic acid, and with Barker North methylphosphorous acid. With J. W. Rodger he investigated thiophosphoryl trifluoride, and they subsequently carried out a long research on the viscosity of miscible liquids and solutions of gases.

In 1894 Thorpe left South Kensington to become Director of the Government Laboratory, for the new buildings of which, in Clements Inn, he was largely responsible. He remained in this post until his retirement in 1909, when

he resumed for three more years the Chair of Chemistry at the Royal College of Science at South Kensington, then merged, along with the City and Guilds Institute, in the newly constituted Imperial College of Science and Technology. The new chemical laboratories in the Imperial Institute Road were built while he was at the Government Laboratory, but he had spent much time with the writer in getting out the first plans, which were finally finished and carried out under the direction of his successor, Sir William Tilden. It must have been a great delight to him to see them completed and to take command again of the Chemistry Department in these fine new laboratories.

His tenure of the headship of the Government Laboratory brought him more into contact with analytical, pharmaceutical and industrial chemical problems, and his papers during this time naturally assumed this aspect. For instance, with J. Holmes, he published papers concerning the occurrence of paraffins in tobacco leaf and on the estimation of ethyl alcohol in essences and medicinal preparations; with C. Simmonds he collaborated on lead silicates in pottery manufacture. Pure chemistry, however, was not forgotten, for he determined the atomic weight of radium, a most important piece of work, which more than ever exemplified his exceptional dexterity of manipulation and accuracy of work. After his return to South Kensington he also undertook, with A. G. Francis, another atomic weight redetermination, that of strontium.

Thorpe had received the honour of a C.B. in the year 1900, and on his retirement from the Government Laboratory he was knighted. He finally retired from the Imperial College Chair in 1912, with the title of Emeritus Professor, and beyond advisory work for the Government during the war his later years have been devoted to literary work. The first edition of his great 'Dictionary of Applied Chemistry' had appeared in 1890, while he was at the Royal College of Science, and after passing through several intermediate editions and reprints was in process of undergoing revision for a new and enlarged edition, five of the seven volumes of which he lived to complete, and which have since been published. Besides this monumental and highly useful work in several volumes, published by Messrs. Longmans, and his early well-known text-books on 'Inorganic Chemistry' (Collins, 1873), 'Quantitative Analysis' (Longmans, 1870), and 'Qualitative Analysis' (Longmans, 1871), his literary efforts include the publication of his Gilchrist Lectures on 'Coal and its Uses' (1878), and a series of delightful books on historical and biographical chemistry. The latter include 'Essays in Historical Chemistry' (Macmillan, 1894), 'History of Chemistry' (Watts, 1909), 'Humphry Davy, Poet and Philosopher' (Cassell, 1896), 'Joseph Priestley' (Dent, 1906), and the 'Right Hon. Sir H. E. Roscoe' (Longmans, 1916). Moreover, he published two books for yachtsmen, 'A Yachtsman's Guide to the Dutch Waterways' (Stanford, 1905), and 'The Seine from Havre to

Paris' (Macmillan, 1913), for his great recreation was yachting, in which he took delight almost up to the last, the writer having been out to sea with him on his visit in July, 1923. This pastime proved a highly serviceable one during the magnetic survey, especially as regards the determinations on and near the Scottish coast and lochs. Indeed, it was largely with the view of being able to use his two yachts (the third larger one having perforce been left at Gothenburg on the outbreak of war in 1914), that he settled at Salcombe, the fine estuary there being so particularly suitable for his purpose.

Although scarcely more than half of Thorpe's scientific memoirs have been specifically referred to, sufficient will have been said to indicate the immense number, importance and scope of his original scientific investigations. While essentially a chemist, his outlook was never narrow, and not at all confined even to Science in general, for he was greatly interested in Art, being a connoisseur of pictures of no mean order. Moreover, he had a very large circle of Continental friends. It was to him, for instance, that Mendeléeff invariably came first on arriving in England, as the writer has occasion well to remember, having had the honour of receiving him once when he came totally unexpected, more or less of a refugee, practically without luggage, and at a time when Sir Edward was not immediately to be found. Indeed, Thorpe probably understood that great but somewhat erratic man and master mind better than anyone in this country, and was more than kind on the occasions when Mendeléeff was in trouble.

One further side of Sir Edward's life, his great public services and those to the scientific societies, still remains to be dealt with. Besides having served on many Royal Commissions and Departmental Committees, he served three periods (1890-91, 1893-95, and 1899-1903) on the Council of the Royal Society, and acted as Foreign Secretary from 1899 to 1903 and as Vice-President in 1894-95. He was awarded a Royal Medal in 1889. Becoming a Member of the Chemical Society in 1870, he served as Treasurer for ten years (1889-99), and as President from 1899 to 1901. He was the first recipient of the Society's Longstaff Medal, on its creation in 1881. He also delivered to the Society, at the Council's invitation, the Memorial Lectures to Kopp and Victor Meyer. He was President of the Society of Chemical Industry in 1895. He was also President of the Chemical Section of the British Association at their Leeds meeting in 1890, and President of the Association itself at the Edinburgh meeting in 1921, as already mentioned. He was also a very active member of the International Committee on Atomic Weights. Honours were showered upon him, for, besides many foreign ones, he received the Honorary Degrees of Sc.D. from Dublin University, of D.Sc. from Manchester and Leeds Universities, and of LL.D. from the Universities of Edinburgh and Glasgow.

An able and incisive speaker, compelling attention (in spite of his short stature) both by his resonant voice and his always interesting matter, a

brilliant lecturer and experimenter, a faithful teacher, who never failed to make himself clearly understood, and an original investigator of keen penetration, infinite resource, consummate manipulative skill, scrupulous accuracy and its ever-accompanying quality of neatness, Sir Edward Thorpe not only inspired those who had the good fortune to study under him, but impressed the honourable mark of thoroughness and trustworthiness on the department of British Science which he so well represented. The spirit of research ever emanated from him and vivified all his teaching, and it may be hoped, and indeed believed, that its leaven has quickened the spirits of a band of devoted students, striving to emulate his fine example and to work for the honour of British Science and the acquirement of true knowledge for its own sake, throughout the whole of the Empire. Though his bodily presence has passed from us, this noble influence and high example must remain undying and permanent.

A. E. H. T.

HORACE TABBERER BROWN—1848-1925.

HORACE TABBERER BROWN was born at Burton-on-Trent, on July 20, 1848, and died on February 5, 1925. His father, Benjamin Tabberer, a man of yeoman stock, died before his birth, and his mother married Edwin Brown, of Burton, whilst he was still an infant. At his stepfather's wish he assumed the surname by which he was subsequently known. He always spoke in terms of great affection of his stepfather, who was a naturalist of the old school in the best sense of the word, and his wide knowledge of entomology, botany and geology doubtless exercised a strong influence on Horace in his early days. He was fortunate in his early schoolmasters, and from boyhood he imbibed a love of classics which stood him well through his whole life. He must have been an essentially interesting lad, for he, with little outside help, started on the study of physics and astronomy at a very early age, but his great interest lay in chemistry, and he determined that his life's work should lie in the pursuit of this branch of science. He came under the influence of Peter Griess, the chemist to Messrs. Allsopp & Sons, while still a boy. After leaving school, he went in the spring of 1865 to the Royal College of Chemistry in London, where, though his stay was but brief, he worked under Hoffmann and later under Frankland. Here he made the acquaintance of Cornelius O'Sullivan (who



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afterwards became chemist to Messrs. Bass & Co.), and also of H. E. Armstrong, who was a fellow student and for whom he entertained lively feelings of affection throughout his life.

He had always intended to enter the brewing industry, and as an opening offered at Messrs. Worthington's Brewery, he left the College of Chemistry before he had completed his first year, taking up the Burton appointment early in 1866.

The work of a "junior brewer" in those days was not a light one—and few young men at the present day who embark on a scientific industrial career would relish a twelve-hour day, alternating with twelve-hour night duty periods, at a salary beginning at £50 and rising to £90 in the fifth year. This period was one of apprenticeship to the mysteries of the business of a brewer, for in those days empiricism was held in much, and science in very little, regard. However, Brown did not give up the pursuit of science, even under the strenuous conditions of his daily (or nightly) work; and later on he was given some "laboratory" facilities in connection with the analysing of water, the salts occurring in which were believed to play a very important part in the quality of the beer. These investigations took him into the field of geology, and in the late eighties he published a valuable memoir on the Permian Rocks of the Leicestershire Coalfield ('Quart. Jour. Geol. Soc.,' 1889).

It was about this time that he commenced the serious studies on the physiology of germination which did so much towards the elucidation of the complex problems underlying the art of successful brewing. He was especially qualified for these investigations, both by his chemical knowledge and his keen interest in the botanical aspects of the matter. He had already made a name for himself as a pioneer in the investigation of the behaviour of the carbohydrates, and was elected a Fellow of the Royal Society in 1889. In the following year he read before the Chemical Society a joint paper, by himself and G. H. Morris, on "Researches on the Germination of some of the Gramineæ." He used to regard this as one of the most important of his contributions to science, and it certainly marked a great advance in current knowledge of what went on during the process of malting. Probably, however, most of his later contemporaries would put his achievement in elucidating the processes of diffusion on a much higher plane, though no doubt the *practical* importance of the earlier research was very considerable.

Another piece of work of great interest was his determination of the reason why the addition of hops to newly racked beer should act in starting a secondary fermentation in the cask. The discovery of the existence in the hops of a very small amount of enzyme, capable of hydrolysing the residual dextrine substances, was a valuable one, and showed the insight of the man. He went on to attack the much larger problem of the synthesis of carbohydrates in the green leaf, and in 1893, again in conjunction with Morris, published a memoir

on the Chemistry and Physiology of Foliage Leaves which was a very fine piece of work, even if all the conclusions therein reached have not commanded universal acceptance.

Shortly after the publication of this paper he severed his connection with the Burton Brewery, and ultimately decided to settle in London, where he spent the remainder, and, from the point of view of scientific output, perhaps the most productive period, of his life. He continued to publish papers dealing with the carbohydrates and their transformations within the plant, and it was in connection with the study of photosynthetic processes that he encountered the problem which he solved so brilliantly, and in connection with which his name will always occupy an assured place in the annals of important scientific discovery.

It had long been a matter of difficulty to explain how the plant could so efficiently utilise the small amount of carbon dioxide present in the air, and the difficulty was emphasised as it became clear that the stomata of the green parts were its sole normal means of entrance into the interior of the plant. Brown brought all his genius for investigation to bear on the subject, and finally established and explained the mode in which the actual rate of diffusion through the stomata takes place.

The research involved a reconsideration of the operation of the laws of diffusion, as then generally accepted, and it afforded a complete solution of all the difficulties that had continually presented themselves. Incidentally, also, it afforded another illustration of the marvellous way in which structure and function in the living organism are correlated, and how admirably the plant is fitted to perform these functions as a machine constructed on sound (though not always obvious) physical and mechanical principles. Perhaps one day we shall reach an equally intelligible explanation of other physical or "physiological" operations, such as root-pressure and the like.

The general results of his research on diffusion were embodied in a Friday evening lecture given at the Royal Institution on March 22nd, 1901, a lecture which was perhaps as fine as any which has ever been delivered within its walls.

Brown made other excursions into the physics of photosynthesis, as may be seen from the list of his published papers in the "Society's Catalogue of Papers." It is not surprising that his scientific work met with recognition. He was awarded the Longstaff Medal of the Chemical Society in 1894, a Royal Medal (1903) and the Copley Medal (1920) by the Royal Society, and the University of Edinburgh admitted him in 1898 to the Degree of LL.D. *Hon. Causa.*

His interests were not confined to this country, for he embarked on fruit growing and vine cultivation in South Africa, having purchased in 1901 a fruit and wine farm in Cape Colony. The estate was primarily intended for

his younger son, though after the death of the latter in 1909 it was still kept on till the War interrupted the visits which, in company with his wife, Brown used to make to it during the period of the northern winter. He introduced great improvements in wine making, and indeed it was a source of gratification to him that the wine from Beyers Kloof was among the best that South Africa has produced, a verdict the soundness of which those who have enjoyed his hospitality would easily admit.

Dr. Brown managed, in spite of his other pursuits, to engage in various works in the public interest. He was a member of the Royal Commission on Whiskey and Potable Spirits, under the chairmanship of Lord James of Hereford in 1908, and in the next year represented the brewers on an investigation initiated by the Board of Inland Revenue for the purpose of determining the original gravities of beers. He served as War Treasurer, and subsequently as Foreign Secretary of the Chemical Society, and was for some years Treasurer of the Lawes Agricultural Trust at Rothamsted. He also represented the Royal Society on the Governing Body of the Imperial College of Science and Technology.

Brown was fortunate in his married life, but the death of his wife in 1915 was a severe blow to him. Soon after the War, failing health compelled him to relinquish his public duties, together with his scientific work, and he turned in his last years more and more to a study of the Latin classics for which he had always retained a lively interest. As a man he possessed a personality of peculiar charm which, coupled with his wide range of interests, attached to him a circle of devoted friends.

J. B. F.

G. D. LIVEING—1827-1924.

By the death of Dr. George Downing Liveing the Society has lost one of its oldest members. He died on 26th December, 1924, shortly after his 97th birthday, and had been a Fellow of the Society since 1879.

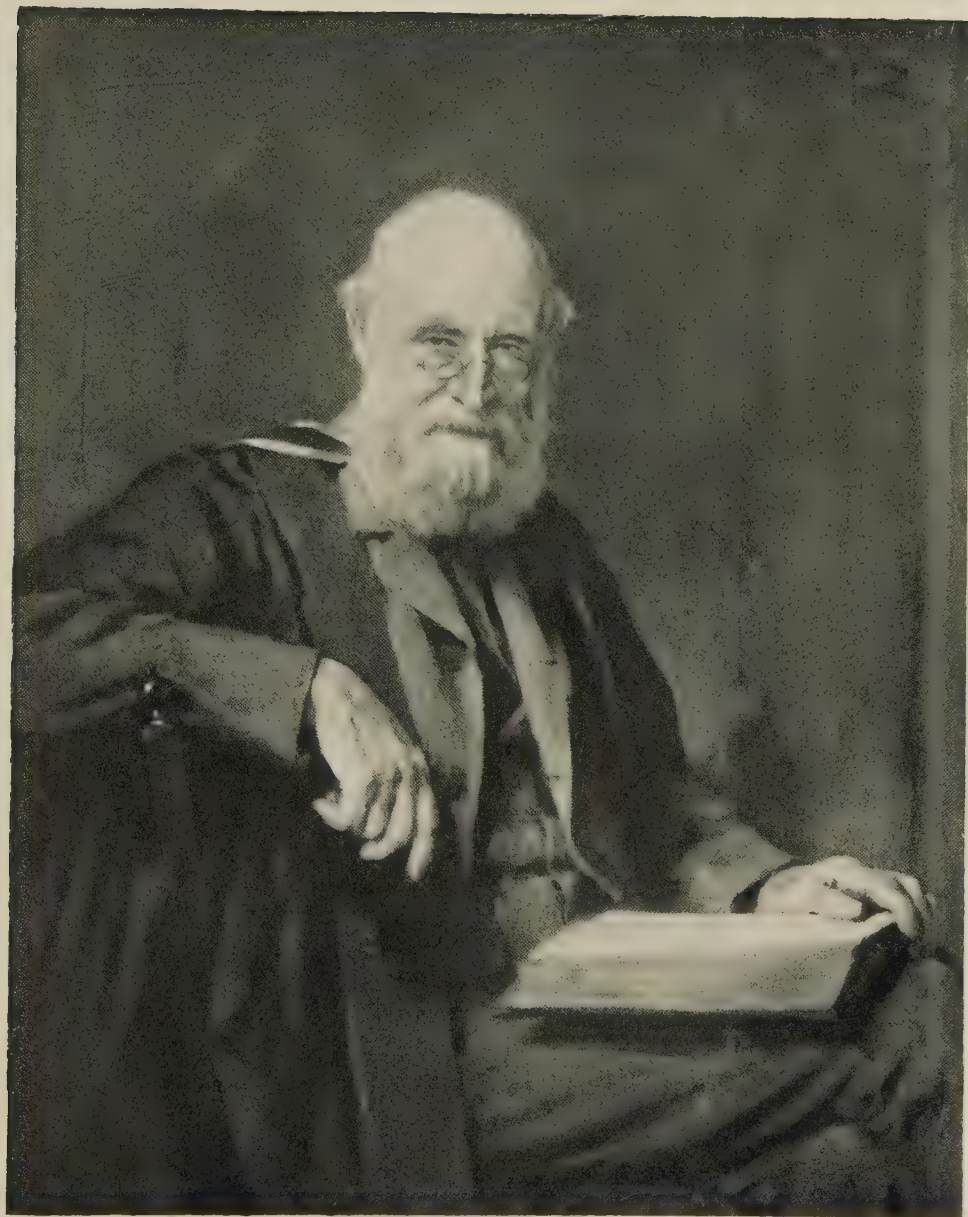
The eldest son of Edward Liveing, of Nayland, in Suffolk, he was entered at St. John's College, Cambridge, in 1847. He was 11th Wrangler in 1850, and in 1851 his name appeared at the head of the first class of the Natural Sciences Tripos. The examination was held for the first time in that year, and Liveing obtained distinction in Chemistry and Mineralogy.

After working for a few months in Berlin under Rammelsberg, he was made a Fellow and Lecturer of St. John's College, and the story of his work is intimately bound up with the story of the rise of the Cambridge School of Natural Science.

Shortly after his return to Cambridge, Liveing was asked by the Regius Professor of Physic to give a course of lectures on chemistry to the medical students. Having agreed to do this, he rented a small cottage for the purpose and fitted it at his own expense. After a year or so, however, his college built him a small laboratory, and on the death of the Reverend James Cumming in 1861 Liveing was appointed to the Professorship of Chemistry, a post which he held till his retirement in 1908.

With characteristic enthusiasm Liveing at once emphasised the importance of the University widening its range of study beyond the traditional limits of Classics, Mathematics, Theology and Medicine; his efforts were backed by a group of distinguished contemporaries—Whewell, Adam Sedgwick, W. H. Miller, Humphry and Stokes—and a scheme was accordingly brought forward for building laboratories and lecture rooms on the site of the old Botanic Garden. The chemical laboratory was to be "constructed underground; it was to be capable of resisting violent explosions and to be as little inflammable as possible." These suggestions were promptly rejected by Liveing, who proceeded to equip and maintain a small laboratory at his own expense. Here he carried on his practical work until 1888, when the University at length recognised the importance of his disinterested labours by providing him with a laboratory which was, at the time, the finest in the country.

Meanwhile, in 1875, James Dewar had been appointed Jacksonian Professor of Natural Philosophy. Liveing and Dewar were men of widely different temperaments and widely different ideals; and they were both quick-tempered. Nevertheless, a close lifelong friendship was formed between them, and their joint work, concerned almost entirely with spectroscopy and extending over the years 1878-1900, was fortunately collected into a single volume and published by the University Press in 1915. This book is a remarkable testimony of



G. D. Living

Liveing's care and skill as an experimenter and to his patience as an accurate observer. Much of our present knowledge and theory of spectroscopy, and especially of the reversal of the spectral lines, has its origin in the results recorded in Liveing's papers, and he was awarded the Davy Medal by the Royal Society in 1901.

Apart from his purely scientific work, Liveing had a keen sense of civic duty. He took an active part in academic and municipal work, and for some years held a commission in the Cambridge Rifle Corps. His judgment as a magistrate was constantly sought by his colleagues on the bench when a difficult case was before them.

In 1885 he published a small book on *Chemical Equilibrium the Result of the Dissipation of Energy* which attracted a great deal of attention, and his last paper on *The Recuperation of Energy in the Universe* was published as late as 1923. For some years he was engaged on experimental research in this subject in the Department of Metallurgy, and he was on his way to the laboratory on 11th October, 1924, when he met with the accident which was to prove fatal some two months later.

Clear and concise as a lecturer, Liveing found it difficult to accept the new views of chemical constitution which developed with such rapidity during the period of his professorship. In the laboratory he was a strict disciplinarian, and students, feeling him to be difficult of approach, did not always get the full benefit of his immense store of accurate knowledge. But those who had the privilege of deeper intimacy with him realised that beneath his austerity of manner there was not only a rich fund of humour and anecdote but a warm heart which was always ready with sympathy in times of difficulty and trouble.

C. T. H.

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